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α-Linked Bifuran and α,α′-Linked Tricycles Containing Furan and/or Thiophene. EPR Investigations and Electrochemical Behavior

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The radical cations from 5,5′-dimethyl-2,2′-bifuran **(1)** and 5,5″-dimethyl-2,2′,5′,2″-terfuran **(5)**, and from the α,α′-linked triheterocycles containing thiophene and furan, bis(5-methyl-2-furyl)-thiophene **(6)** and bis(5-methyl-2-thienyl)furan **(7)**, were generated in fluid solution with trifluoroacetic acid (TFA) or mixtures of TFA and 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP), in the presence or absence of thallium(III) trifluoroacetate as oxidant, and analyzed by electron paramagnetic resonance. The hyperfine coupling (hc) constants were assigned by comparison with those from 5,5′-dimethyl- **(3)** and 5,5′-di-*tert*-butyl-2,2′,5′,2″-terthiophene **(4)** and by investigation into the deuterated species generated in solution with deuteriotrifluoroacetic acid and, in the case of $\mathbf{5}^{\bullet+}$, $\mathbf{6}^{\bullet+}$, and $\mathbf{7}^{\bullet+}$ confirmed by theoretical calculations. The parent compounds **1**, **5**, **6**, and **7** were synthesized by known procedures. Cyclic voltammetry of them in dimethylformamide using tetrabutylammonium hexafluorophosphate or perchlorate as electrolyte display irreversible oxidation peaks. The anodic peak for the oxidation of terfuran **5** is lower than that of bifuran **1**, and anodic peaks for the oxidation of the trimers with furan rings **6** and **7** are lower than those for terthiophenes **3** and **4**.

Introduction

Organic conducting polymers have been the subject of a major research activity during recent years.[2,3] In particular, polythiophene and its derivatives have proved to be good candidates due to their electric and nonlinear optical properties and excellent environmental stability.[2,4] All these polymers exhibit their attracting properties in the oxidized state, when the development of polarons (radical cations) and bipolarons (dications) along the polymeric chains gives rise to defects in their π-electronic configuration.[5]

Analysis of spin density distribution in the radical cations of small constituent oligomers of polythiophene helps in understanding the distribution of polarons over the polymer's backbone. For this reason, we have systematically investigated the electronic structure of such models during recent years by means of electron paramagnetic resonance (EPR) spectroscopy which is an excellent technique for studying the properties of semioccupied molecular orbitals (SOMO).[6]

The choice of the best system to prepare radical cations is difficult,[7] although in aromatic five-membered heterocycles such as furans, thiophenes, and pyrroles, trifluoroacetic acid (TFA) in the presence of mercury(II) or thallium(III) trifluoroacetate has been used extensively.[6a,b,8] If the oxidation potentials of the aromatic substrates are lower, as in oligomers, dimers, and trimers of thiophene, mere solution of the substrates in TFA, diluted or not with an inert and stabilizing solvent such as CH_2Cl_2 or 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP),[9] is sufficient to generate the radical cations.[6c,h,10]

Radical cations of furans, thiophenes, and pyrroles, when dissolved in those systems, have been easily detected by EPR only when the adjacent positions to the heteroatom in these rings are blocked by alkyl substituents. Otherwise, the oxidized species are very unstable and oligomerize through their more active extreme

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positions.[6a,b] However, when 2,2′-bithiopenes, the most simple oligomers of thiophene, are involved, not only the 5,5′-dialkyl derivatives display good and strong EPR spectra corresponding to their radical cations, but also 3,3′-dialkyl derivatives with unsubstituted extreme positions develop spectra attributed to their shorter-lived radical cations.[6h,i] However, the regioisomers 4,4′-dialkyl-2,2′-bithiophenes develop in acidic medium spectra which were assigned the structures of the 5,5′-bisprotonated radical cations.[6i] In the unsubstituted parent compound, the 2,2′-bithiophene, its radical cation is so unstable that it is not detected, and spontaneously oligomerizes, resulting a single and broad line in the EPR.

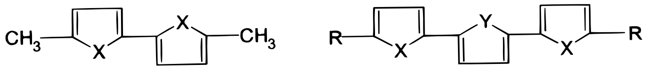
Recent interest has also been directed toward the synthesis of copolymers composed by different conjugated ring systems in the main chain.[11] The diverse electronic properties of the constituents of these materials open the possibility for developing novel electronic structures, such as intramolecular charge transfer. In this way, we have investigated the molecular and electronic structure of some small cooligomers with thiophene and pyrrole, and we have reported the EPR spectrum of the *N*-hexyl-2,5-di(2-thienyl)pyrrole radical cation. This radical cation, without substituents in its reactive extreme positions, is stable enough to show a sufficiently well-resolved spectrum which is easy to characterize.[12]

Among the polyheterocyclic polymers of pyrrole, thiophene, and furan, polyfuran have received much less attention because of the difficulty to prepare it in good quality.[13] Only very recently, an extensive characterization on this material have been reported.[14]

Attracted by the great interest in the theoretical and experimental results on this kind of organic oligomers and cooligomers, herein we extend our EPR spectroscopy and electrochemical studies to other dimers and trimers, such as 5,5′-dimethyl-2,2′-bifuran **(1)** and 5,5″-dimethyl-2,2′,5′,2″-terfuran **(5)**, the most simple oligomers of polyfuran, as well as to two mixed and symmetric α,α′-linked triheterocycles, bis(5-methyl-2-furyl)-2,5-thiophene **(6)** and bis(5-methyl-2-thienyl)-2,5-furan **(7)**. The results of these studies have been analyzed and compared with those obtained from the oligomers of thiophene, 5,5′-dimethyl-2,2′-bithiophene **(2)**, and 5,5″-dimethyl- **(3)** and 5,5″-di-*tert*-butyl-2,2′,5′,2″-terthiophene **(4)**.

Synthetic Results

The α,α′-linked heterocycles containing furan and/or thiophene, **5**, **6**, and **7** were obtained by known procedures. Reaction of 2 equiv of aryllithium with *N*,*N*,*N*′,*N*′-tetramethylsuccinimide at low temperature afforded the corresponding 1,4-diaryl-1,4-butanediones **8** and **9**.[15] Diketone **8** was subsequently made to react with acetic anhydride and concentrated sulfuric acid to give terfuran **5**,[16,17] with an excellent yield, and with Lawesson's reagent to give quantitatively tricycle **6**. Diketone **9** with acetic anhydride and concentrated hydrochloric acid gave tricycle **7**, also with an excellent yield[17] (Scheme 1).



(1): X = O

(2): X = S

(3): X = Y = S, R = CH$_3$

(4): X = Y = S, R = *t*-Bu

(5): X = Y = O, R = CH$_3$

(6): X = O, Y = S, R = CH$_3$

(7): X = S, Y = O, R = CH$_3$

Electron Paramagnetic Resonance Results

5,5′-Dimethyl-2,2′-bifuran (1). Figure 1a shows an excellent EPR spectrum of the radical cation of bifuran **1** which was observed by photolyzing at 263 K the substrate in the presence of trifluoroacetic acid (TFA). A spectrum of similar quality was observed when **1** was photolyzed in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) with TFA (10%). Concerning radical cations in fluid solution, the asymmetry of their EPR spectra, with regard to the value of the field in the central point of the spectrum, corresponds to the presence of two or more different doublet species in the medium with different *g* values. In this particular case, the spectrum in Figure 1a does not show practically asymmetry, but the small hyperfine splitting displayed by some peaks, shown as two very overlapped doublets, is evidence of the presence of two very similar radical cations with the same *g* value, which must correspond to the presence of two different conformations of the molecule, *syn* and *anti*, similarly as it is observed in the bithiophene series.[6c,10a] A computer simulation of the spectrum is shown in Figure 1b, using the hyperfine splitting (hfs) constants, peak-to-peak line width (ΔH_{pp}), and approximate abundances of both isomers as reported in Table 1. The average *g* value for both doublets is $g_{av} = 2.0022$, and the best fitting spectrum, as a combination of the spectrum of each doublet, assumes no variation in gauss of the *g* values. The greater proportion corresponds most probably to the thermodynamic more stable conformer, *anti*. Similarly in the bithiophene series, the barrier to free rotation between *syn* and *anti* in the radical cations of bifurans is sufficiently large for both conformers to be observed separately by EPR, and there is no variation in the relative abundance of them in the short range of temperatures tested. The average *g* value is very close to that of the free electron and slightly different from the *g* value of the corresponding bithiophene **2**. It is worth noting that the values of the coupling constants in the radical cation of **1** are slightly larger than those observed for the corresponding radical cation of **2**, also displayed in Table 1.

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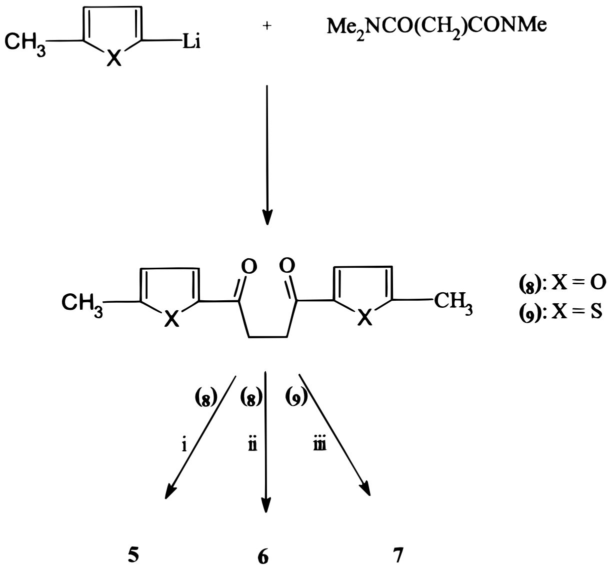
Scheme 1[a]



[a] Reagents: (i) acetic anhydride–H_2SO_4; (ii) Lawesson's reagent, toluene; (iii) acetic anhydride–aqueous HCl acid.

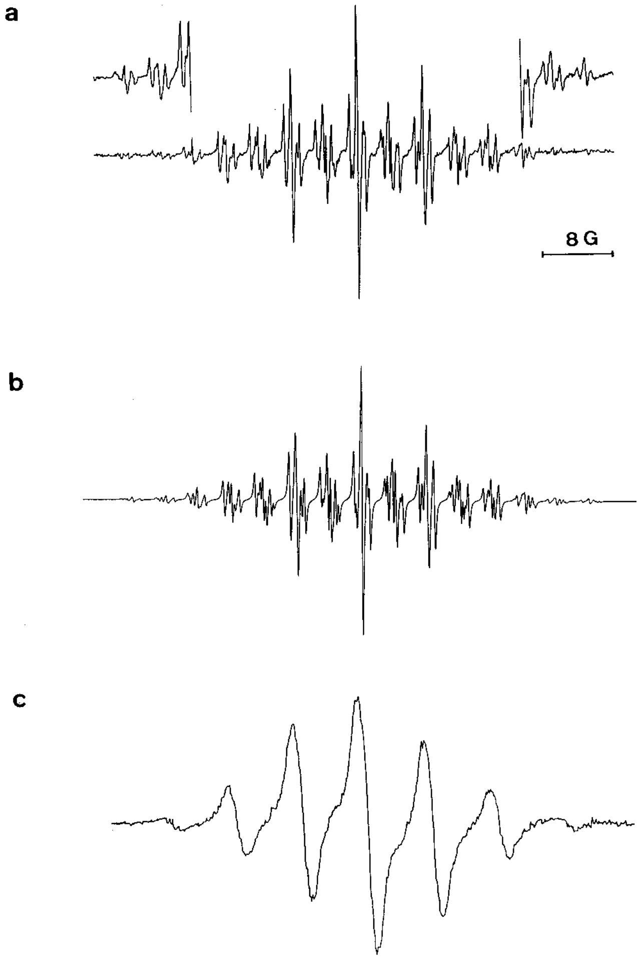


Figure 1. (a) EPR spectrum of an irradiated solution of 5,5′-dimethyl-2,2′-bifuran **(1)** in TFA at 263 K with a modulation amplitude, MA = 0.05. (b) Computer simulation using the data in Table 1. (c) EPR spectrum of an irradiated solution of **1** in deuterated TFA.

A method to facilitate the characterization of complex EPR spectra of doublet species in small oligomers is the selective chemical deuteration of aromatic positions in the neutral compounds. In this way, the unambiguous assignment of the hyperfine coupling constants of the radical cation of 5,5″-dimethyl-2,2′,5′,2″-terthiophene has been achieved by EPR spectroscopy.[10d] On the other hand, exhaustive deuteration of all the aromatic positions occurs when using deuteriotrifluoroacetic acid as solvent in the detection of the radical cations of 5,5′-dimethyl-2,2′-bithiophene and 5,5″-dimethyl-2,2′,5′,2″-terthiophene.[10c] In our case, the spectrum of **1** in deuteriotrifluoroacetic acid is depicted in Figure 1c. This can be easily simulated as a broad (ΔH_{pp} = 2.1 G) septet pattern due to the six methyl protons (a_{6H} = 9.3 G), if it is assumed that all the ring protons have been rapidly exchanged for deuterium atoms and that the splitting from deuterium nuclei only contributes to broadening the signals (magnetogyric ratio relation, $\gamma_H/\gamma_D = 6.514$).

Table 1. EPR Parameters[a] **for Radical Cations from Dimers 1 and 2**

dimer	percent	$a_{3,3'}$	$a_{4,4'}$	$a_{5,5'}$	g	ΔH_{pp}
1	60	4.85	1.1	9.3 (6H)	2.0022	0.2
	40	5.0	0.8	9.5 (6H)		
2[b]	67	3.91	0.94	9.1 (6H)	2.0028	0.1
	33	4.12	0.70	9.2 (6H)		

[a] hc constants and ΔH_{pp} (peak-to-peak line width) in gauss. [b] EPR parameters from ref 6c.

5,5″-Dimethyl- (3) and 5,5″-Di-*tert*-butyl-2,2′,5′,2″-terthiophene (4). We could observe the spectrum of the radical cation of terthiophene **3** in TFA containing mercury(II) or thallium(III) trifluoroacetate at 263 K, or in HFP with TFA (10%) at room temperature (rt). But the best resolved spectrum, which was asymmetric due to the presence of at least two different conformers with slightly different *g* values, was displayed using only TFA as both solvent and oxidant. To simplify the spectrum to get a satisfactory analysis, the complex spectrum of Figure 2a is converted into the symmetric and much simpler one depicted in Figure 2b, employing a larger modulation amplitude. Although this spectrum has been previously observed by other authors,[10b–d] its simulation is displayed in Figure 2c and the average hfs constants, corresponding to the different conformomers, are indicated in Table 2, in order to compare it with the spectra observed for the trimers **5**, **6**, and **7**.

The spectrum of radical cation $\mathbf{4}^{\bullet+}$, which is formed when compound **4** is photolyzed in TFA at 263 K, is shown in Figure 3c, where a mixture of two conformers with slightly different *g* values are observed. If mercury(II) trifluoroacetate is added to the TFA, the concentration of magnetic species is increased and the resolution of the stronger spectrum (Figure 3a) is lower. Because of the great difficulty to simulate the asymmetrical spectrum, the simulation (Figure 3b) has been performed in the less ressolved one using the data in Table 2. So, the hfs constants are averaged out from the values of each conformer. The spin densities in carbons 3,3″ and 3′,4′ are very similar to the corresponding ones in terthiophene **3**, and the small value of the coupling constant associated with the hydrogens in 4,4″ is selected in the same order as the β-hydrogens in 5,5″ positions.

Despite using mercury(II) trifluoroacetate in TFA to generate the radical cations of terthiophenes **3** and **4**, no mercuri-deprotonation occurs as shown by the absence of the satellite bands due to ^{199}Hg hyperfine coupling. These bands do appear in many aromatic substrates when the corresponding radical cations are generated. The mercuriated derivatives, obtained by electrophilic

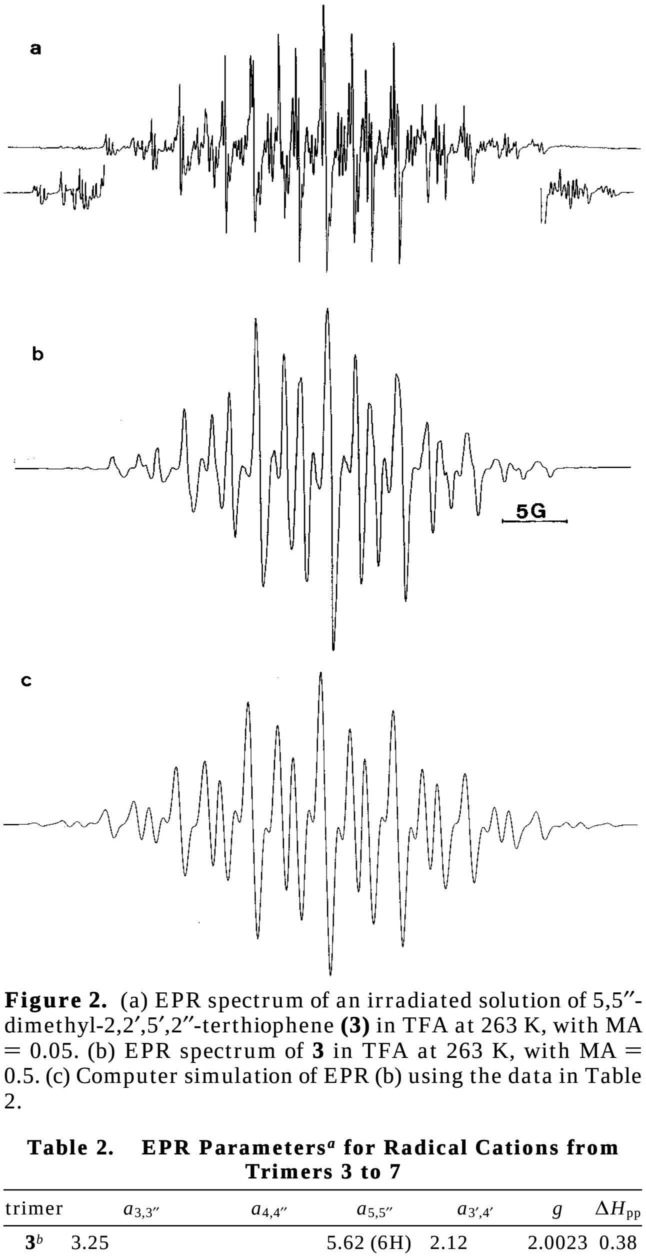


Figure 2. (a) EPR spectrum of an irradiated solution of 5,5″-dimethyl-2,2′,5′,2″-terthiophene **(3)** in TFA at 263 K, with MA = 0.05. (b) EPR spectrum of **3** in TFA at 263 K, with MA = 0.5. (c) Computer simulation of EPR (b) using the data in Table 2.

Table 2. EPR Parameters[a] for Radical Cations from Trimers 3 to 7

trimer	$a_{3,3''}$	$a_{4,4''}$	$a_{5,5''}$	$a_{3',4'}$	g	ΔH_{pp}
3[b]	3.25		5.62 (6H)	2.12	2.0023	0.38
4	3.12		0.18 (20H)	2.25	2.0024	0.11
5	3.95 (4.2)	≈0.35 (0.1)	5.60 (6H) (4.9)	2.60 (3.6)	2.0024	0.10
6	70%: 4.17 (4.4) 30%:4.17 (1H); 4.13 (1H)	≈0.22 (0.3) 0.61 (1H); 0.26 (1H)	5.96 (6H) 5.96 (6H) (5.0)	1.94 (3.2) 1.97 (1H); 1.92 (1H)	2.0019	0.08
7	2.75 (2.8)	≈0.25 (0.1)	5.50 (6H) (4.6)	2.25 (2.4)	2.0026	1.25

[a] hc constants and ΔH_{pp} (peak-to-peak line width) in gauss. Theoretical coupling constants for $\mathbf{5}^{\bullet+}$, $\mathbf{6}^{\bullet+}$, and $\mathbf{7}^{\bullet+}$ are in parentheses. [b] Other EPR parameters in refs 10b–d.

substitution, show a similar range of oxidation potentials, and, therefore, their corresponding radical cations also appear in the same condition. However, only in very few cases have mercuriated radical cations been observed in heterocyclic chemistry.[7,18] Similarly, although thallium(III) trifluoroacetate has been extensively used to generate the radical cations of oligomeric thiophenes, no thallation of the heteroaromatic rings has been observed so far.[7]

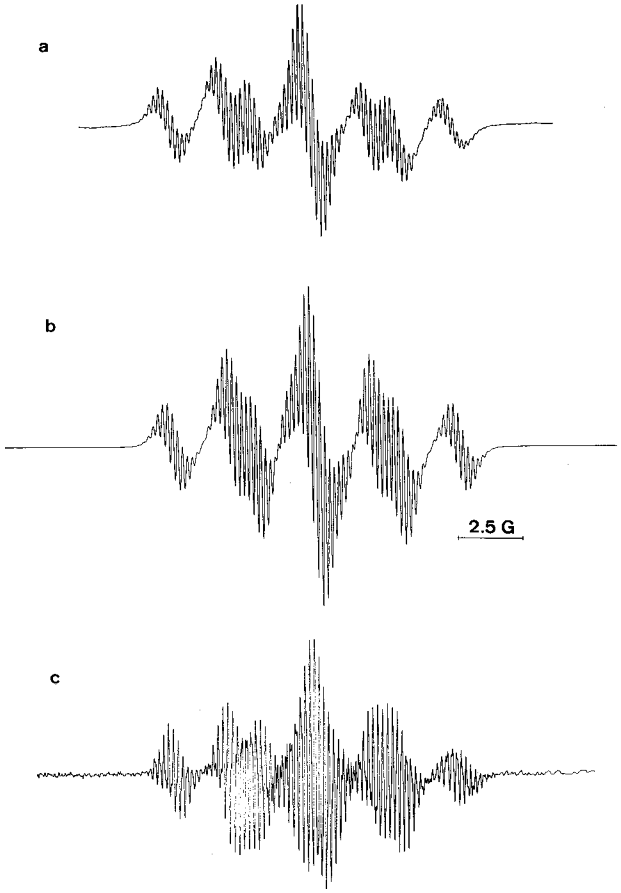


Figure 3. (a) EPR spectrum of a solution of 5,5″-di-*tert*-butyl-2,2′,5′,2″-terthiophene **(4)** in TFA after adding $Hg(OCOCF_3)_2$ at 263 K, with MA = 0.05. (b) Computer simulation of EPR (a) using the data in Table 2. (c) EPR spectrum of a solution of **4** in TFA before adding Hg(II) as oxidant.

5,5″-Dimethyl-2,2′,5′,2″-terfuran (5). The strong EPR spectrum of the radical cation of terfuran **5** in an irradiated HFP solution containing TFA (10%) at rt and the simulated spectrum using the hfs constants in Table 2 are illustrated in Figure 4, a and b, respectively. The assignments of these values to the different hydrogens of the molecule were attributed by comparing them with those unambiguously assigned for terthiophene **3**,[10d] and confirmed by theoretical results.[19] As it has been noted, the spectrum is symmetric and only one doublet species is considered in the simulation. Comparing the spectra of $\mathbf{5}^{\bullet+}$ with those of the radical cations of terthiophenes **3** and **4**, the hfs constants with hydrogens in the 3,3′,4′,3″ positions for $\mathbf{5}^{\bullet+}$ are slightly higher than those for $\mathbf{3}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$. If deuteriotrifluoroacetic acid is used as solvent, a rapid proton–deuterium exchange occurs in all aromatic positions, and the spectrum in Figure 4c is then observed. This spectrum shows a broad septet (a_{6H} = 5.75 G; ΔH_{pp} = 2.15 G) which corresponds to the six methyl protons.

A satisfactory explanation of the spectrum displayed by $\mathbf{5}^{\bullet+}$ is that it is composed of the time-averaged values of the hyperfine couplings of two conformers, the *anti*–*anti* and the *anti*–*syn* or the *syn*–*anti*, or three conformers, considering the less thermodynamically favorable conformation *syn*–*syn* as well. Solutions of **5** in TFA showed the same spectra at 263 and at 293 K, denoting that the conformers are in a rapid dynamic equilibrium

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(19) Spin densities for the radical cations $\mathbf{5}^{\bullet+}$, $\mathbf{6}^{\bullet+}$, and $\mathbf{7}^{\bullet+}$ were computed with the MNDO semiempirical method[20] using the Gaussian 94 computer program.[21] Electron spin densities were transformed into *hfc* values using the McConnell equation.[22]

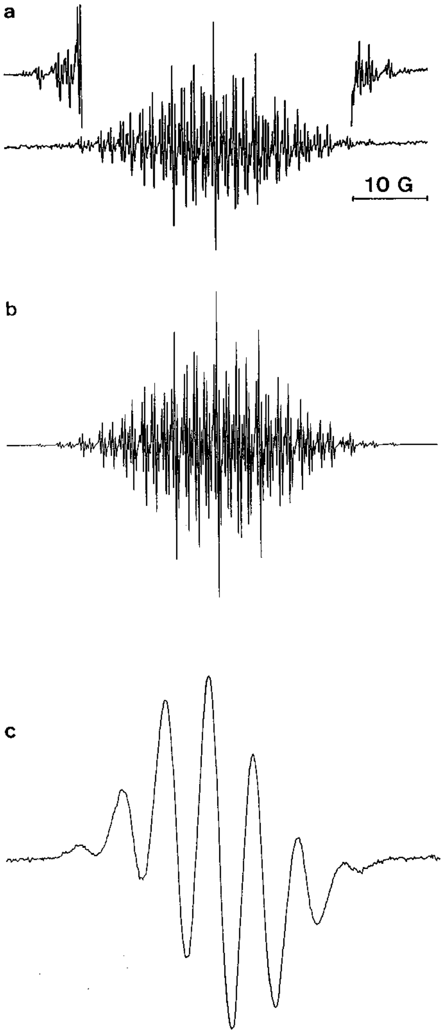

Figure 4. (a) EPR spectrum of an irradiated solution of 5,5″-dimethyl-2,2′,5′,2″-terfuran **(5)** in HFP−TFA (10%) at rt, with MA = 0.0125. (b) Computer simulation using the data in Table 2. (c) EPR spectrum of a solution of **5** in deuterated TFA at rt, with MA = 0.25.

in the medium, and the energy barriers between them are low. On the other hand, the intensity of the signal diminishes on decreasing the temperature in such a way that at 263 K the signal is approximately 60% as intense as at 293 K and the process is reversible. This observation, known for the oligomers of the thiophene series, can be associated with the formation at low temperatures of doubly charged singlet dimers which are not active in the EPR.

Bis(5-methyl-2-furyl)-2,5-thiophene (6). When **6** is photolyzed either in HFP containing TFA (10%) at rt or in TFA at 263 K, a strong and well-resolved spectrum of its radical cation $\mathbf{6}^{\bullet+}$ is observed (Figure 5a). The spectrum can be simulated (Figure 5b) using the hfs constants in Table 2. The best simulation predicts the presence of two conformers, most probably the *anti*−*anti* and the *anti*−*syn* or the *syn*−*anti*, with no appreciable differences in their *g* values, as corresponds to a practically symmetric spectrum. Theoretical calculations[19] support the assignments given in Table 2. An inspection of this table clearly reveals significant increases in the couplings to H-3, H-3″, H-5, and H-5″ and reductions in the couplings to H-3′ and H-4′, when they are compared with those for the radical cation of terthiophene **3**, and, consequently, the spin density in $\mathbf{6}^{\bullet+}$ is shifted to the furan rings with regards to $\mathbf{3}^{\bullet+}$.

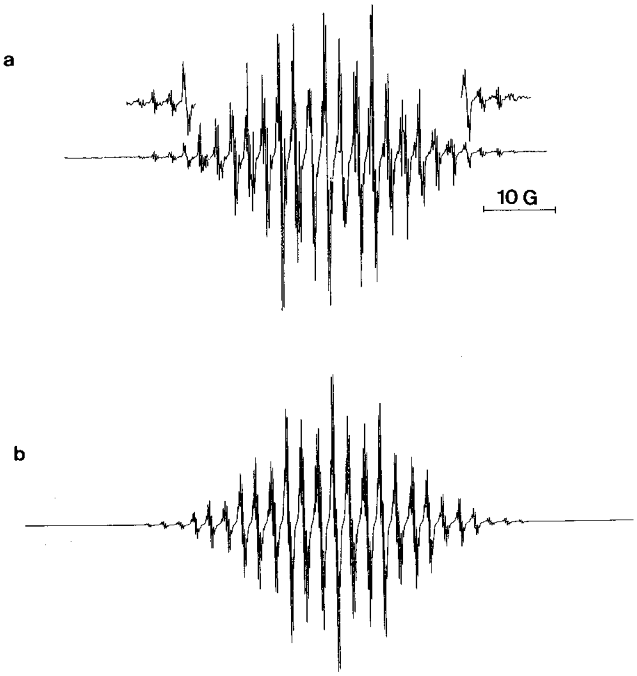

Figure 5. (a) EPR spectrum of an irradiated solution of 2,5-bis(5-methyl-2-furanyl)thiophene **(6)** in HFP−TFA (10%) at rt, with MA = 0.04. (b) Computer simulation using the data in Table 2.

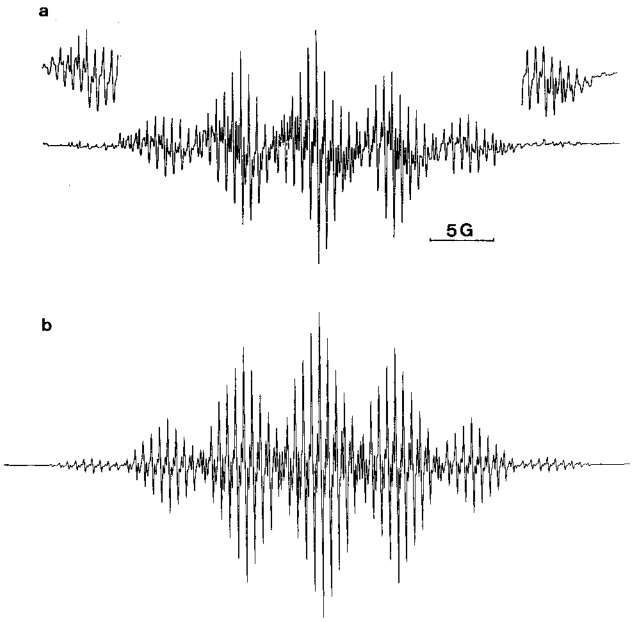

Figure 6. (a) EPR spectrum of an irradiated solution of **6** in deuterated TFA at rt, with MA = 0.02. (b) Computer simulation using the data in the text.

When deuteriotrifluoroacetic acid was used as solvent, the spectrum of Figure 6a is observed. The best computer simulation predicts also the presence of two conformers, yielding the following hfs constants: 70%, *a*(5,5″) = 6.0 (6H), *a*(3,3″) = 0.64 (2D), *a*(3′,4′) = 1.94 (2H); 30%, *a*(5,5″) = 6.0 (6H), *a*(3,3″) = 0.64 (2D), *a*(3′,4′) = 1.94 (1H), 1.50 (1H); *g* = 2.0022 for both conformers. It should be noted that hydrogens in C-3′ and C-4′ have not been exchanged for deuteriums and the values of their hfs constants are as above except in one hydrogen that drops to 1.50 G. Thus, selective deuteration takes place in the more basic

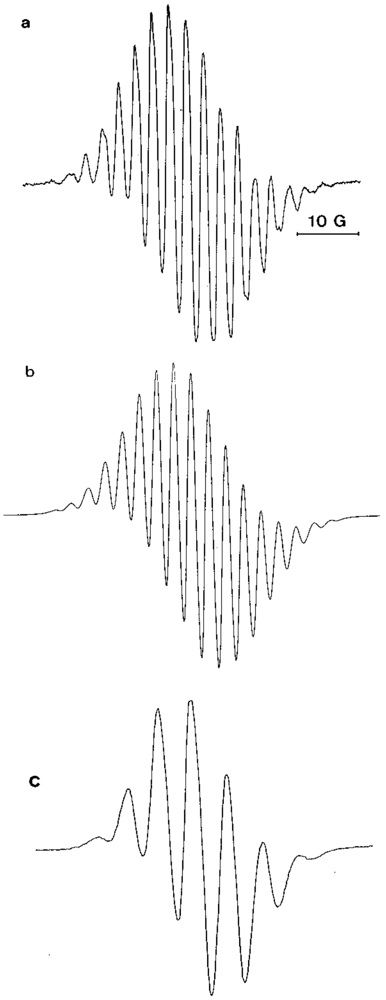

Figure 7. (a) EPR spectrum of a solution of 2,5-bis(5-methyl-2-thienyl)furan **(7)** in TFA at rt, with MA = 0.063. (b) Computer simulation using the data in Table 2. (c) EPR spectrum of a solution of **7** in deuterated TFA at 263 K, with MA = 0.04.

aromatic positions. The values of the hfs constants for deuterium in 3 and 3″ positions are those expected considering the magnetogyric ratio relation, $\gamma_H/\gamma_D = 6.514$ (1.94/6.514 = 0.64 G).

Bis(5-methyl-2-thienyl)-2,5-furan (7). When **7** is dissolved in trifluoroacetic acid or in HFP containing TFA (10%) at rt, it exhibited the EPR spectrum of $7^{\bullet+}$, whose intensity and resolution (ΔH_{pp} = 1.25 G) did not appreciably increase by irradiation (Figure 7a). The spectrum is symmetric and was simulated (Figure 7b) considering only one doublet species in the medium and using the hfs constants displayed in Table 2. The couplings to H-3 and H-3″ are reduced and the couplings to H-3′ and H-4′ are increased compared with those couplings for the radical cation $3^{\bullet+}$, and, consequently, the spin density in $7^{\bullet+}$ is shifted to the central furan ring with regard to $3^{\bullet+}$. Furthermore, rapid exchange of all ring protons occurs in deuteriotrifluoroacetic acid (Figure 7c), resulting in a broad septet pattern (a_{6H} = 5.25 G; ΔH_{pp} = 2.5 G) due to the six methyl protons.

Cyclic Voltammetry. All compounds were investigated by cyclic voltammetry (CV). They displayed irreversible peaks in the cyclic voltammograms carried out on a Pt electrode from solutions of the substrates (~10^{-3} M) in dimethylformamide (DMF) using tetrabutylammonium hexafluorophosphate (TBAHFP) (0.1 M) or tetrabutylammonium perchlorate (TBAP) as electrolyte. An SSCE (NaCl−aqueous saturated calomel electrode) was used as reference electrode; all potentials given in the text refer to this electrode.

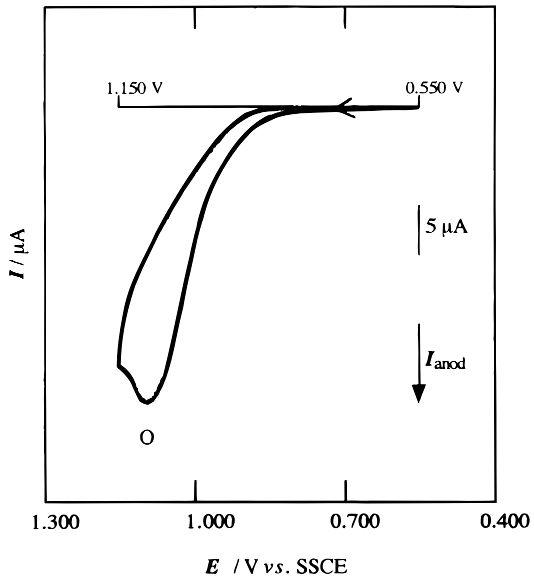

Figure 8. Cyclic voltammogram for the oxidation of a 1 mM 5,5′-dimethyl-2,2′-bifuran solution in 0.1 M TBAHP + DMF on Pt: initial and final potential, 0.550 V; reversal potential, 1.150 V; scan rate, 50 mV s^{-1}; temperature 25 °C.

Table 3. CV Results for the Oxidation on Pt of Dimers and Trimers in DMF (10^{-3} M) at a Scan Rate of 50 mV s^{-1} and at 25 °C

oligomer	background salt	$E^a_p(O_1)$ (V)[a]	$E^a_p(O_2)$ (V)[b]
1	0.1 M TBAHPF	1.08	
2	0.1 M TBAP	1.21	
3	0.1 M TBAP	1.05	1.18
4	0.1 M TBAP	1.10	1.19
5	0.1 M TBAHPF	0.93	
6	0.1 M TBAHPF	0.92	
7	0.1 M TBAHPF	1.01	1.37

[a] Anodic peak potential for either the solt peak or the first oxidation peak. [b] Anodic peak potential for the second oxidation peak.

Cyclic voltammograms of the dimers, 5,5′-dimethyl-2,2′-bifuran **(1)** and 5,5′-dimethyl-2,2′-bithiophene **(2)**, exhibited a single well-defined irreversible oxidation peak O_1. This anodic peak for **1** at a scan rate (*v*) of 50 mV s^{-1} is displayed in Figure 8. A similar single anodic peak O_1 was found for 5,5″-dimethyl-2,2′,5′,2″-terfuran **(5)** at all scan rates tested. In the case of bis(5-methyl-2-furanyl)-2,5-thiophene **(6)**, a single oxidation peak O_1 was also detected up to 50 mV s^{-1}, but at higher *v* values, it became ill-defined, since it overlapped with an emergent second oxidation peak O_2, the height of which increased at higher scan rate. For bis(5-methyl-2-thienyl)-2,5-furan **(7)** and 5,5″-di-*tert*-butyl- **(4)** and 5,5″-dimethyl-2,2′,5′,2″-terthiophene **(3)**, two well-defined and consecutive oxidation peaks, O_1 and O_2, were always recorded by CV. The E^a_p values of the anodic peaks determined at the scan rate of 50 mV $s^{-1}$are summarized in Table 3.

For all compounds, the height of the corresponding peak O_1 increased linearly with the square root of the scan rate, indicating that it is diffusion-controlled.[23] In addition, the difference between its anodic peak and half-

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peak potentials, ($E^a_p - E^a_{p/2}$), was always found to be between 60 and 80 mV, whereas E^a_p varies linearly with log v with a slope close to 30 mV per decade. These results agree with the theoretically expected values for a first-order EC mechanism at 25 °C:[23,24] ($E^a_p - E^a_{p/2}$) = 59.2 mV, slope of E^a_p *vs* log v linear plot = 29.6 mV per decade. This mechanism involves the reversible one-electron oxidation of substrate (electrochemical reaction), followed by an irreversible chemical reaction of the initially electrogenerated radical cation, which is the rate-determining step. According to the above kinetic behavior, the following electrode process is proposed for the oxidation of all substrates (**A**) in peak O$_1$:

$$\mathbf{A} \rightarrow \mathbf{A}^{\bullet+} + 1e$$

$$\mathbf{A}^{\bullet+} \rightarrow \text{products}$$

where $\mathbf{A}^{\bullet+}$ denotes the corresponding radical cation. This species is unstable in the medium and decomposes to more stable products, probably by reaction with the small amount of water present in the DMF.[24] No polymers were formed as final products, since no polymeric deposit was observed on the Pt electrode throughout the CV experiments.

The CV behavior of the second oxidation peak O$_2$, detected for several trimers, is difficult to explain. This peak is much lower than its first oxidation peak and its maximum is usually a plateau. Peak O$_2$ is associated with the oxidation of electroactive products proceeding from the respective $\mathbf{A}^{\bullet+}$, although the possibility that it corresponds to the direct oxidation of $\mathbf{A}^{\bullet+}$ to the dication $\mathbf{A}^{2+}$ cannot finally be ruled out.

The oxidative capability of the substrates can be directly compared from the E^a_p values of their corresponding anodic peak O$_1$, asuming that the decay rates are the same in all cases. As it is shown in the Table 3, oligomers with furan rings have less positive potential values than oligomers with thiophenes. In addition, as other authors have observed for the series of oligothiophenes without substituents,[25] trimers are more easily oxidable than dimers, either in the thiophene or furan series.

Conclusions

We have detected for the first time the radical cations of 5,5′-dimethyl-2,2′-bifuran (**1**) and 5,5″-dimethyl-2,2′,5′,2″-terfuran (**5**), as well as the radical cations of two mixed and symmetric α,α′-linked triheterocycles, the bis(5-methyl-2-furyl)-2,5-thiophene (**6**) and the bis(5-methyl-2-thienyl)-2,5-furan (**7**) by means of EPR spectroscopy and cyclic voltammetry. The stability of these oxidized species, which allows their detection and characterization by EPR as multiplets due to the coupling of the unpaired electron with hydrogens in the molecule, is a consequence of the presence of methyl substituents blocking their more reactive extreme positions; otherwise they easily polymerize in the medium, as shown with 2,2′-bithiophene and 2,2′,5′,2″-terthiophene in which case a single and broad peaks corresponding to different oligomeric fractions appear in the spectra.

All these compounds display irreversible peaks in their cyclic voltammograms which correspond to the oxidation of the parent compounds to their radical cations, with anodic potentials lower in trimers than in dimers due to the greater extension of the electronic conjugation. An analysis of the these potentials displayed in Table 3 also shows that bifuran **1** has a lower value than bithiophene **2**, and the trimers with furan rings present slightly lower values than the terthiophenes **3** and **4**. Thus, oligomers with furan rings, despite the greater electronegativity of the heteroatom, oxygen *versus* sulfur, are more easily oxidable than the corresponding oligomers with only thiophene rings. At first sight, these results seem to be unexpected, but they can be accounted for by the lower aromaticity of furan than thiophene. In this context, Tamao *et al*. have shown by *ab initio* calculations that the HOMO of furan is slightly higher in energy than the HOMO of thiophene.[11d] These results are also supported by the EPR spectra of the radical cations of the bifuran **1** and terfuran **2**. Both spectra give hfs constants of the unpaired electron with hydrogens in the molecule a little higher than the corresponding ones in the thiophene series (Table 2) and, therefore, the spin density of the unpaired electron in sulfur is greater than in oxygen. These differences might suggest that the contribution of the less electronegative heteroatom, sulfur, in the electronic configuration of the HOMO in the parent diamagnetic heterocycles, bithiophene **2** and terthiophenes **3** and **4**, is greater than the contribution of oxygen in bifuran **2** and terfuran **5**, respectively. On the other hand, if an analysis of the hfs constants with hydrogens in the thiophene rings of $\mathbf{6}^{\bullet+}$ and $\mathbf{7}^{\bullet+}$ with regard to those of $\mathbf{3}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ is made, one can realize that those constants are lower in the first ones and, therefore, the π-electrons of the HOMO reside largely in the furan rings. These results open the possibility for developing intramolecular charge transfers in the polymers constituted by furan and thiophene rings.

Experimental Section

Melting points were obtained by using a Köfler microscope "Reichert" and are uncorrected. The IR spectra were recorded with a Perkin-Elmer 683 spectrometer, and the ^{1}H NMR spectra were determined at 200 and 300 MHz and the ^{13}C NMR spectra at 50 and 75 MHz with Varian Gemini 200 HC and XL-300 spectrometers, respectively.

The cyclic voltammetry measurements for all compounds were carried out in a 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 connected to the cell through a salt bridge containing a 0.1 M TBAHFP + DMF solution. Cyclic voltammograms were recorded with standard equipment consisting of an Inelecsa potentiostatic system connected to a Philips 8043 $X-Y$ recorder. Scan rates ranging

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between 20 and 200 mV s^{-1} were studied. The volume of all test solutions was 25 cm^3. The temperature was kept at 25 °C.

EPR spectra were recorded using a Varian E 109 spectrometer working in the X-band and using a Varian E−257 temperature-controller. The EPR simulations were carried out with the WinSIM program from the National Institute of Environmental Health Sciences (NIEHS). Diluted solutions of the oligomers in the appropiate solvent with or without oxidant were degassed by passing a stream of dry argon through the solution to remove oxygen before introducing the solutions into the cavity of the spectrometer. Photolysis into the cavity was performed by using an Oriel 500-W high pressure mercury arc without filters. Constant irradiation is necessary to retain signals; if not, they slowly decay. The solvents 1,1,1,3,3,3-hexafluoropropan-2-ol and deuteriotrifluoroacetic acid were used as received, and trifluoroacetic acid was distilled before use.

5,5′-Dimethyl-2,2′-bifuran **(1)** was synthesized by the oxidative coupling of lithium di(5-methylfur-2-yl)cuprate, in accord with the literature.[26] 5,5″-Dimethyl-2,2′,5′,2″-terthiophene **(3)** was synthesized using the Ullmann procedure by generating the dianion of α,α′-terthiophene and quenching with CH_3I.[26] 5,5″-Di-*tert*-butyl-2,2′,5′,2″-terthiophene **(4)** was prepared by a Friedel−Crafts reaction on α,α′-terthiophene catalyzed by $AlCl_3$.[27]

Bis(5-methyl-2-furyl)-1,4-butanedione (8). A solution of *n*-butyllithium (41.2 mL; 1.6 M in hexane) was added slowly at −20 °C and in an inert atmosphere (Ar) to a solution of 2-methylfuran (4.8 g; 60 mmol) in dry ether (130 mL), and the mixture was warmed to rt and stirred for 4 h. The solution was cooled at 0 °C and *N*,*N*,*N*′,*N*′-tetramethylsuccinimide (5.0 g; 29 mmol) was added in one portion. The reaction mixture was stirred at rt for 24 h. The solution was cooled in an ice bath and 10% HCl (150 mL) was added slowly. After stirring for 1 h, the ethereal layer was separated. The aqueous layer was extracted with $CHCl_3$. The combined organic layers were washed successively with water and brine solution, and the organic phase was dried over Na_2SO_4 and filtered; the solvent was removed under reduced pressure. The solid obtained was chromatographed over silica gel using CH_2Cl_2 as eluant to give bis(5-methyl-2-furyl)-1,4-butanedione (3.0 g; 42%) as a yellow solid: mp 101−3 °C (from CH_2Cl_2−hexane); ^1H NMR ($CDCl_3$) δ 2.40 (s, 6H), 3.23 (s, 4H), 6.16 (dd, 2H, $J_A = 2.2$ Hz; $J_B = 0.6$ Hz), 7.17 (d, 2H, $J_A = 2.2$ Hz); IR (KBr) 3100 (m), 2980 (w), 2920 (w), 1660 (s), 1640 (s), 1580 (w), 1510 (s), 1445 (m), 1410 (m), 1370 (w), 1360 (m), 1330 (m), 1265 (m), 1220 (m), 1200 (m), 1085 (w), 1055 (s), 1035 (s), 1025 (s), 990 (w), 975 (m), 950 (m), 920 (m), 825 (m), 800 (m), 775 (m), 705 (w), 660 (w), 630 (w), 615 (w); MS. *m*/*e* (relative intensity) 246 (18), 164 (7), 137 (41), 109 (100). Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.3; H, 5.7. Found: C, 68.4; H, 5.8.

5,5″-Dimethyl-2,2′,5′,2″-terfuran (5). Concentrated H_2SO_4 (5 drops) was added to a stirred solution of bis(5-methyl-2-furyl)-1,4-butanedione (1.96 g; 8.0 mmol) in acetic anhydride (32 mL) and then stirred for an additional 30 min. The solution was poured into ice−water and stirred for 1 h. The solid was extracted with $CHCl_3$ and the organic layer, washed successively with saturated Na_2CO_3 solution and water, was dried giving a residue which was chromatographed over silica gel using CCl_4 as eluant to give 5,5″-dimethyl-2,2′,5′,2″-terfuran (0.33 g; 18%): mp 96−7 °C (lit.[13] 91 °C) (from methanol); ^1H NMR ($CDCl_3$) δ 2.36 (s, 6H), 6.04 (dq, 2H, $J_A =$ 2.2 Hz; $J_B = 0.6$ Hz), 6.49 (d, 2H, $J_A = 2.2$ Hz), 6.51 (s, 2H); ^{13}C NMR ($CDCl_3$) (76 MHz) 151.6, 147.6, 131.9, 122.0, 107.7, 105.9, 13.6; IR (KBr) 3120 (m), 2990 (w), 2930 (w), 2910 (m), 2870 (w), 1580 (s), 1450 (s), 1380 (w), 1290 (m), 1210 (w), 1190 (s), 1085 (m), 1020 (s), 1005 (m), 980 (w), 950 (s), 875 (s), 780 (s).

Bis(5-methyl-2-thienyl)-1,4-butanedione (9). A solution of *n*-butyllithium (82.5 mL; 1.6 M in hexane) was added slowly at −20 °C and in an inert atmosphere (Ar) to a solution of 2-methylthiophene (11.78 g; 120 mmol) in dry ether (100 mL), and the mixture was warmed at rt for 2 h. The solution was cooled at 0 °C and *N*,*N*,*N*′,*N*′-tetramethylsuccinimide (10 g; 58 mmol) was added in one portion. The reaction mxture was stirred at rt for 40 h. The solution was cooled in an ice bath, quenched with 10% HCl (250 mL), and stirred for 1 h. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$. The combined organic layers were washed successively with water and brine solution, dried over Na_2SO_4 and filtered, and the solvent was removed at reduced pressure. The residue obtained was chromatographed over silica gel using CH_2Cl_2 as eluant to give bis(5-methyl-2-thienyl)-1,4-butanedione (5.35 g; 33%) as a yellow solid: mp 179−180 °C (from ether); ^1H NMR ($CDCl_3$) δ 2.54 (s, 6H), 3.31 (s, 4H), 6.81 (d, 2H, $J = 3.8$ Hz), 7.62 (d, 2H, $J = 3.8$ Hz); IR (KBr) 2920 (m), 1650 (s), 1450 (s), 1435 (s), 1410 (m), 1370 (m), 1320 (s), 1220 (s), 1185 (s), 1155 (m), 1055 (s), 980 (m), 935 (s), 810 (m), 805 (m), 780 (s), 700 (m), 660 (w) cm^{-1}. Anal. Calcd for $C_{14}H_{14}O_2S_2$: C, 60.4; H, 5.1; O, 11.5; S, 23.0. Found: C, 60.4; H, 5.1; O, 11.7; S, 23.0.

2,5-Bis(5-methyl-2-thienyl)furan (6). Concentrated hydrochloric acid (6 mL) was added slowly to a mixture of bis-(5-methyl-2-thienyl)-1,4-butanedione (1.01 g; 3.63 mmol) and acetic anhydride (50 mL). The reaction mixture was stirred for 4 h at rt and then poured into water and extracted with $CHCl_3$. The organic solution was washed successively with saturated $NaHCO_3$ solution and water, and then dried over Na_2SO_4. The solvent was evaporated and the residue was purified by chromatoghaphy over silica gel with $CHCl_3$ as eluant to give 2,5-bis(5-methyl-2-thienyl)furan (0.80 g; 84%) as a yellow solid: mp 75−6 °C; ^1H NMR ($CDCl_3$) δ 2.49 (d, 6H, $J_A = 1$ Hz), 6.42 (s, 2H), 6.68 (dq, 2H, $J_B = 3.6$ Hz, $J_A =$ 1 Hz), 7.07 (d, 2H, $J_B = 3.6$ Hz); ^{13}C NMR ($CDCl_3$) (76 MHz) 148.3, 138.8, 131.2, 125.8, 122.4, 106.2, 15.2; IR (KBr) 3100 (w), 3075 (w), 2910 (m), 2850 (w), 1605 (m), 1525 (s), 1440 (m), 1370 (m), 1310 (w), 1270 (w), 1225 (m), 1185 (s), 1155 (m), 1050 (m), 1025 (m), 990 (m), 960 (m), 795 (m), 780 (s), 755 (s), 750 (s), 660 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{12}OS_2$: C, 64.6; H, 4.7; O, 6.1; S, 24.6. Found: C, 64.5; H, 4.6; O, 6.3; S, 24.6.

2,5-Bis(5-methyl-2-furyl)thiophene (7). A mixture of diketone **9** (1.66 g; 6.73 mmol) and Lawesson's reagent (1.69 g; 4.04 mmol) in toluene was refluxed for 24 h. The toluene was evaporated and the residue was chromatographed over silica gel using hexane−CH_2Cl_2 (1:1) as eluant to give 2,5-bis-(5-methyl-2-furyl)thiophene (1.64 g; quantitative) as a yellow oil; ^1H NMR (CDCl3) d 2.34 (s, 6H), 6.01 (dq, 2H, $J_A = 3.2$ Hz, $J_B = 0.6$ Hz), 6.37 (d, 2H, $J_A = 3.2$ Hz), 7.07 (s, 2H); ^{13}C NMR ($CDCl_3$) 151.6, 147.6, 131.9, 122.0, 107.7, 105.9; IR (KBr) 3100 (m), 2980 (w), 2940 (w), 2910 (m),2860 (w), 1605 (w), 1565 (s), 1550 (m), 1495 (w), 1430 (s), 1370 (w), 1270 (m), 1210 (m), 1190 (m), 1060 (w), 1030 (m), 1010 (s), 940 (m), 885 (w), 870 (m), 790 (s), 765 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.8; H, 5.0; O, 13.1; S, 13.1. Found: C, 68.7; H, 5.1; O, 12.9; S, 13.1.

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