

Thallium(III) Trifluoroacetate–Trifluoroacetic Acid in the Chemistry of Polythiophenes. 2. Treatment of 3-Alkylthiophenes and Electron Paramagnetic Resonance Results

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The treatment of thiophene and 3-alkylthiophenes with thallium(III) trifluoroacetate (TTFA) in trifluoroacetic acid (TFA) gives insoluble and dark powdery solids with oxygen content and electrical conductivities ranging from 10^{-4} to $10^{-6} \Omega^{-1} \text{cm}^{-1}$. Polar and short fractions are negligible. All of them show semiconductivity (10^{-3} – $10^{-6} \Omega^{-1} \text{cm}^{-1}$) when doped in iodine atmosphere. Electron paramagnetic resonance (EPR) spectra of either as-synthesized or I_2 -treated solids display characteristic single and broad lines (ΔH_{pp} , 1.84–7.4 G) with Lorentzian shapes and g -values in the range 2.0028–2.0038. Infrared spectra show characteristic C–H out-of-plane deformations (780cm^{-1} for polythiophene and 820 – 825cm^{-1} for poly(3-alkylthiophenes)) in addition to a strong peak at 1650 – 1690cm^{-1} which has not been conclusively assigned. EPR spectra of some disubstituted and tetrasubstituted 2,2'-bithiophene radical cations have been observed and their g -values and coupling constants assigned when the corresponding parent compounds are photolyzed with ultraviolet light in TFA. Photolysis of 3-alkylthiophenes in TFA in the EPR instrument gave the radical cations of 4,4'-dialkyl-2,2'-bithiophenes. In no case, were EPR signals of the isomeric 3,3'-dialkyl- or 3,4'-dialkyl-2,2'-bithiophene radical cations observed, indicating that dimerization of 3-alkylthiophenes occurs through the less sterically hindered 5-position. The presence of two doublet species corresponding to both conformers, *syn* and *anti*, in the radical cations is associated with a large barrier to rotation about the C(2)–C(2') bond.

Introduction

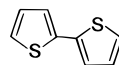
Thallium(III) trifluoroacetate (TTFA)–trifluoroacetic acid (TFA) has been proved to be a good reagent system to generate radical cations of aromatic substrates¹ and particularly, of five-member heterocyclic compounds, when these are conveniently blocked in their most reactive sites, in order to prevent polymerization reactions by oxidative condensation.²

These excellent properties of the TTFA–TFA system are due not only to the stabilization effect of radical cations by TFA but to the low nucleophilicity of the system which prevents any further reaction on the primary radical cations.³ Thus, if mercury(II) trifluoroacetate, also a good oxidant, is used instead of thallium(III) trifluoroacetate, some substrates undergo, after being oxidized to their radical cations, further mercuriation on the aromatic ring.⁴ However, there is no report of the observation of the analogous thallation reaction in experiments with TTFA. Sometimes, when aromatic substrates have low oxidation potentials, photolysis of solutions of them in TFA may be sufficient to generate the radical cations.

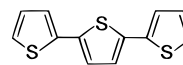
In this context, we have been able to obtain and detect by means of electron paramagnetic resonance (EPR) many radical cations of furans, thiophenes, and pyrroles when they are substituted on their C(2) and C(5) carbons

by alkyl groups. Strong signals with good hyperfine splittings appear in the EPR spectra of these heteroarenes. This technique has proved to be a powerful method of studying the spin distribution in the SOMO.^{2a,b}

More recently, the application of the system TTFA–TFA in 5,5'-dialkyl-2,2'-bithiophenes has generated the radical cations of these simple oligomers. These radical cations are very stable and do not undergo further secondary reactions when solutions of these substrates were conveniently degassed at low temperatures (0°C).⁵ But, if the parent compound, 2,2'-bithiophene (**1**), or 2,2',5',2''-terthiophene (**2**) were treated under the same conditions, doped polymeric fractions with good properties were obtained. This is a good test to confirm that if polymerization in these substrates occurs, it goes by means of oxidative condensation of the thiophene oligomers through the reaction at the sterically unhindered positions of their radical cations.⁶



(1)



(2)

Therefore, TTFA–TFA is also an excellent chemical method of obtaining semiconducting polymers from bithiophenes and terthiophenes. These polymers were characterized by their poor solubility in different organic solvents because of the rigidity of their carbon-backbone chains. We will now report on the results when 3-alkylthiophenes and thiophene itself are treated with this

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Table 1. Chemical Composition of As-Synthesized Samples

monomer	anal., % found				Total	empirical formula ^a
	C	H	S	O		
3	53.3	2.0	34.7	8.6	98.6	C _{4.1} H _{1.8} S _{1.0} O _{0.5}
4	61.3	5.0	27.3	4.7	98.3	C _{6.0} H _{5.8} S _{1.0} O _{0.3}
5	65.2	6.9	22.6	2.8	97.5	C _{7.7} H _{9.7} S _{1.0} O _{0.2}
6	71.3	8.6	17.3	2.6	99.8	C _{11.0} H _{15.8} S _{1.0} O _{0.3}

^a Empirical formulas are estimated by assuming one sulfur atom for repeated unit in the chain.

oxidant system, and we will try to study and characterize the paramagnetic species when these thiophenes, with free 2- and 5-positions, are analyzed by means of EPR spectroscopy.



- (3): R = H
 (4): R = C₂H₅
 (5): R = nC₄H₉
 (6): R = nC₇H₁₅

Treatment of 3-Alkylthiophenes with TTFA-TFA. Synthesis. Thiophene (**3**) and its substituted derivatives, 3-ethyl- (**4**), 3-butyl- (**5**), and 3-heptylthiophene (**6**), were treated with thallium(III) trifluoroacetate in trifluoroacetic acid (1:1, molar proportion) at room temperature. The reactions were left for 24 h and no special precautions were taken to avoid oxygen and moisture during the polymerization. Therefore, the solutions were not degassed by argon bubbling prior to treatment, and only an argon atmosphere was maintained during the processes.

The initial solution turned dark blue immediately after adding the TTFA, and the precipitation of a very fine and dark powder was observed within a few minutes. The composition and the empirical formulae of these powders are displayed in Table 1. All of them show the presence of oxygen in their composition, the highest content being in the sample prepared from thiophene **3**. These results and the analytical characterization of them, mainly by electron paramagnetic resonance and conductivity measurements, suggest that a light oxidation, by the formation of localized polarons or radical cations into the chains, is induced simultaneously during the chemical process.

The oxidized samples were treated with hot ethanol in a Soxhlet extractor to remove polar impurities. Only small quantities of soluble fractions were separated. The composition of the insoluble fractions (Table 2) are slightly different from those of the as-synthesized materials. A change of color is not observed during this process which denotes that the degree of oxidation of the samples remains nearly unchanged. Even if purification with ethanol is followed by extraction with CHCl₃ and chlorobenzene, to remove low and medium molecular weight fractions, respectively, as it was performed with the sample obtained from 3-ethylthiophene (**4**), the separated soluble fractions are very small and the elemental composition of carbon, hydrogen, sulfur, and oxygen of the insoluble part does not differ appreciably from the as-synthesized material.

The low solubilities of the above purified samples show an important difference in the properties of the reported poly(3-alkylthiophenes),⁷ although some authors suggest that the solubility of these polymers is very limited when

operating in optimized conditions.⁸ One of the problems in the samples reported now is the great difficulty in undoping them which might suggest that oxygen is incorporated in the backbone structure as carbonyl groups.

This behavior is completely different from that observed in polythiophenes when longer oligomers, as 2,2'-bithiophenes and 2,2',5',2''-terthiophenes, were used as starting materials and under the same reaction conditions.⁶ Thus, washing these polymers with hot ethanol resulted in a practically complete undoping of the samples, the insoluble products changed their colors from dark brown to reddish brown, and their elemental composition after purification with CHCl₃, THF, and chlorobenzene nearly agreed with those of the neutral polymer, the oxygen content being in negligible proportions.

In the treatment of the thiophene (**3**) with TTFA-TFA, if special care is taken to avoid traces of oxygen in the medium, by argon bubbling the TFA solutions of thiophene and TTFA before mixing them and then keeping the inert atmosphere during the process, the reaction practically does not proceed, and only a very small fraction of insoluble polymer was obtained. If the starting monomer is 3-ethylthiophene (**4**) and the same precautions are taken to avoid oxygen, the reaction goes on, but in the purification process of the obtained sample with organic solvents, the soluble fractions in ethanol, CHCl₃, and chlorobenzene increase in weight. The insoluble final part is approximately 55% of the total. In this case, the composition of the soluble fraction in CHCl₃ (C, 63.3; H, 5.6; S, 26.1; O, 4.0%) and of the insoluble final part (C, 63.2; H, 5.2; S, 26.1; O, 4.1%) are similar to that displayed in Table 2. The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) of the CHCl₃ soluble fraction, determined by gel permeation chromatography, are 12249 and 4483, respectively, which implies a polydispersity of 2.7. This M_n corresponds to an average of 40 thiophenes per chain. Its UV-vis spectrum in CHCl₃ solution has a maximum absorption at about 385 nm, and its ¹H NMR spectrum (Figure 1) displays two separated and broad peaks at 2.59 and 2.83 ppm, corresponding to the position of the methylene groups in the two possible regioisomers in the polymer backbone structure, the head-to-head and the head-to-tail placements.

The purified samples from **3**, **4**, **5**, and **6** were then exposed to iodine vapors at atmospheric pressure to be further oxidized. Analytical data of the resulting solids are given in Table 3. All of them show the presence of variable percentages of iodine and the lowering in the percentages on carbon, hydrogen, and sulfur. In the three substituted thiophenes, the longer the alkyl chain the less the proportion of incorporated iodine. The empirical formulas are those from the purified samples adding the corresponding iodine, and the calculated composition in brackets are estimated from the empirical formulas which are in good agreement with the experimental values.

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Table 2. Chemical Composition of Purified^a Samples

monomer	anal. % found (calcd) ^b					empirical formula
	C	H	S	O	total	
3	53.5 (58.5)	2.0 (2.5)	35.6 (39.0)	8.4	99.6	C _{4.1} H _{1.8} S _{1.0} O _{0.5}
4	62.8 (65.4)	5.1 (5.5)	28.1 (29.1)	3.0	99.0	C _{6.0} H _{5.8} S _{1.0} O _{0.2}
5	67.5 (69.5)	6.8 (7.3)	23.0 (23.2)	2.3	99.6	C _{7.8} H _{9.4} S _{1.0} O _{0.2}
6	71.3 (73.3)	8.5 (9.0)	17.4 (17.7)	2.0	99.2	C _{10.9} H _{15.5} S _{1.0} O _{0.2}

^a Purification by extensive Soxhlet extraction with ethanol (6 h). ^b Calculated as follows: **3**, (C₄H₂S)_n; **4**, (C₆H₆S)_n; **5**, (C₈H₁₀S)_n; **6**, (C₁₁H₁₆S)_n.

Table 3. Chemical Composition of Iodine-Doped Samples

monomer	anal. % found (calcd) ^a				empirical formula ^b
	C	H	S	I	
3	46.9 (47.0)	1.7 (1.8)	31.8 (31.6)	12.2 (12.4)	C _{4.0} H _{1.8} S _{1.0} O _{0.5} I _{0.09}
4	46.1 (46.3)	3.8 (3.8)	20.6 (20.7)	26.9 (26.9)	C _{6.0} H _{5.8} S _{1.0} O _{0.2} I _{0.33}
5	60.6 (60.3)	6.2 (6.1)	20.7 (20.7)	11.4 (11.2)	C _{7.8} H _{9.4} S _{1.0} O _{0.2} I _{0.13}
6	71.0 (71.0)	8.5 (8.5)	17.0 (17.0)	1.5 (1.4)	C _{10.9} H _{15.5} S _{1.0} O _{0.2} I _{0.05}

^a Calculated compositions are estimated from the empirical formulas. ^b Empirical formulas are those of the purified samples in Table 2 by adding the corresponding iodine.

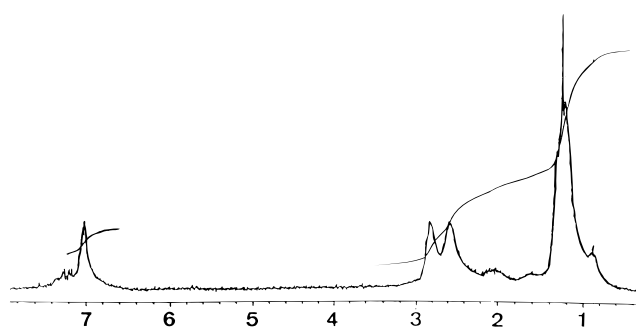


Figure 1. ¹H NMR spectrum of CHCl₃-soluble fraction of poly(3-ethylthiophene).



Figure 2. Infrared spectra in KBr pellets of (a) as-synthesized polymer and (b) I₂-doped polymer from thiophene (**3**).

Infrared (IR) Spectroscopy. As an example, typical IR spectra of purified polythiophene before and after iodine oxidation are displayed in Figure 2. Characteristic broad bands at approximately 1340, 1200, 1110, and 1030 cm⁻¹, corresponding to oxidized polythiophenes, are observed both in the purified and in the iodine-doped polymer. Those bands which have been interpreted on the basis of bipolarons (dications),⁹ are broader and stronger in intensity in the iodine-doped sample than in the purified one.

The principal IR absorption bands observed in the polythiophene and poly(3-alkylthiophenes) and their assignments are presented in Table 4. The bands at 780 cm⁻¹, characteristic of C–H out-of-plane deformation of the 2,5-disubstituted thiophenes, and at 820–825 cm⁻¹, of the 2,4,5-trisubstituted thiophenes, indicate a linear polymer chain structure. The peak assigned to C_β–H stretching in the range 3060–3080 cm⁻¹ is very weak in all of them. Besides the normal peaks corresponding to this kind of polymers, all of them display a strong-medium peak at 1650 cm⁻¹ in the polythiophene and at 1690 cm⁻¹ in the poly(3-alkylthiophenes). This absorption is sometimes assigned to an overtone of the thiophene ring C–H out-of-plane bend.¹⁰ When it is strong, it has been attributed sometimes to the presence of carbonyl groups,¹¹ although some authors have preferred to assign it to the aromatic ring stretching.¹² Concerning the soluble fraction in CHCl₃, when 3-ethylthiophene is treated in TFA with TTFA in a rigorously inert atmosphere as mentioned above, its ¹³C NMR spectrum does not display any peak corresponding to C=O, despite the fact that its IR spectrum presents a strong peak at 1690 cm⁻¹. On the other hand, some preliminary results from the polymerization of 3,4-diethylthiophene with TTFA in TFA under the same conditions show that although the IR spectrum of the polymeric insoluble fraction presents a strong and sharp peak at 1680 cm⁻¹, its elemental analysis does not indicate any traces of oxygen.

Electron Paramagnetic Resonance. EPR spectral data, including *g*-factors and peak-to-peak line widths are summarized in Table 5. The spectra of all the polymeric samples consist of a single and symmetrical line with a Lorentzian shape corresponding to weak-conducting samples. The *g*-values are included in the range 2.0028–2.0038, comparable to that of a free electron (2.0023). This indicates a weak spin-orbit coupling with the sulfur atom, the free electron being mainly delocalized into the carbon backbone structure, as is typical in this type of polymer.

Electrical Measurements. The electrical conductivities of the polymers were measured either in as-synthesized or in I₂-doped samples using compressed

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Table 4. Infrared Band Positions (cm⁻¹) and Their Assignments for Purified Poly(3-alkylthiophenes)

monomer	arom C-H str	aliph C-H str	ring str	methyl def	arom C-H out-of-plane
3	3080		1650	1525, 1490	780
4	3060	2970, 2940, 2880	1690	1515, 1455	1370
5	3070	2965, 2930, 2865	1690	1510, 1450	1375
6	3060	2960, 2920, 2850	1690	1515, 1455	1375

^a IR spectra were recorded in KBr pressed pellets.

Table 5. EPR Spectral Parameters and Electrical Conductivities of Samples Measured at Room Temperatures

monomer	sample	<i>g</i>	ΔH_{pp}^a (G)	σ^b ($\Omega^{-1} \text{ cm}^{-1}$)
3	as-synthesized	2.0035	1.8	3.1×10^{-4}
	I ₂ -doped	2.0036	2.8	2.6×10^{-3}
4	as-synthesized	2.0032	3.6	2.3×10^{-5}
	I ₂ -doped	2.0030	6.3	2.6×10^{-3}
5	as-synthesized	2.0038	5.1	4.6×10^{-6}
	I ₂ -doped	2.0028	6.2	3.0×10^{-4}
6	as-synthesized	2.0037	7.4	2.1×10^{-6}
	I ₂ -doped	2.0031	—	4.7×10^{-6}

^a ΔH_{pp} : peak to peak line width of the first derivative of the absorption curve. ^b σ : conductivity measurements at 20 °C on pressed pellets by the four-probe method.¹³

pellets at 20 °C by the four-probe method.¹³ As it is displayed in Table 5, the longer the alkyl chain of the substituent the lower the conductivity value.

Electron Paramagnetic Resonance on 3-Alkylthiophenes and 4,4'-Dialkyl-2,2'-bithiophenes. Although a variety of methods is available to generate radical cations, we have found a general and excellent procedure to generate heteroaromatic radical cations in fluid solution by photolyzing the substrates in trifluoroacetic acid (TFA) with or without mercury(II) or thallium(III) trifluoroacetate (TTFA) at low temperatures (−10 °C) or even at room temperature.

To shed further light on the behavior of 3-alkylthiophenes in the TTFA–TFA system, we examined very dilute solutions of these monomers in TFA by EPR spectroscopy, irradiating them in the same cavity of the instrument. Therefore, when a solution of 3-ethylthiophene in TFA at −10 °C was irradiated, the spectrum in Figure 3a was obtained. The asymmetry of this spectrum indicates the formation of two doublet species. Photolysis of 4,4'-diethyl-2,2'-bithiophene (**7**) under the same conditions displayed the same spectrum but at higher peak intensity (Figure 3c), although slightly different as for the composition of the two doublet species. All of this suggests that excited 3-ethylthiophene undergoes an oxidative dimerization to the corresponding bithiophene radical cation. The radical cation of 3-ethylthiophene is not stable enough to be detected by EPR. This process is carried out on the least sterically hindered site on the thiophene which corresponds to the 5-position. The presence of two doublets suggests the formation of the radical cations of both conformations, *syn* and *anti*. A computer simulation of the spectrum from 3-ethylthiophene is shown in Figure 3b, using the hyperfine splitting (hs) constants and other EPR parameters reported in Table 6. A small change in the relative amounts of both conformers simulates the spectrum starting from **7**. It is worthwhile to indicate the stability of these species (there is not appreciable variation in the intensity of the signals) and the invariability of the composition of the

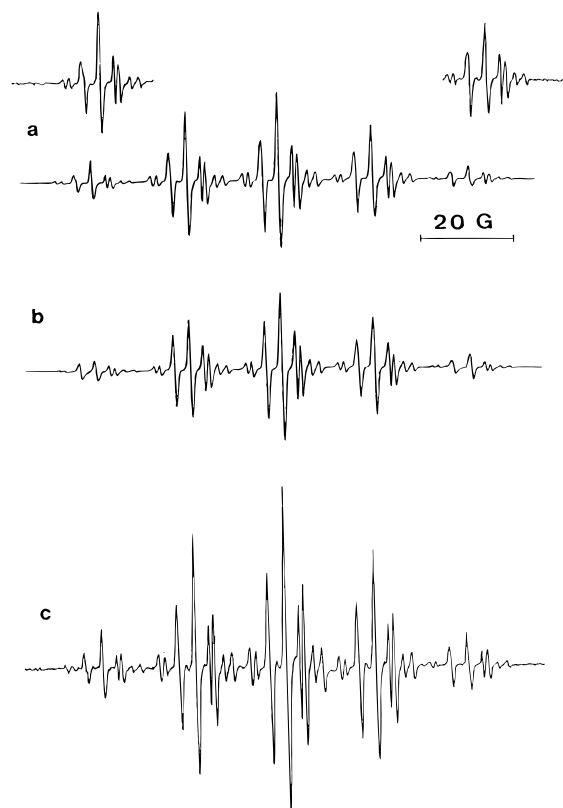


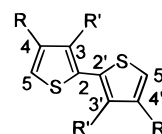
Figure 3. (a) EPR spectrum of an irradiated solution of 3-ethylthiophene (**4**) in trifluoroacetic acid (TFA) at −10 °C. (b) Computer simulation using the parameters given in Table 7 for 4,4'-diethyl-2,2'-bithiophene (**7**) radical cation. (c) EPR spectrum of an irradiated TFA solution of **7** at −10 °C.

Table 6. Experimental Hyperfine Coupling Constants (G) for Radical Cations of 2,2'-Bithiophenes^a

	$a_{3,3'}$	$a_{4,4'}$	$a_{5,5'}$	<i>g</i>	ΔH_{pp} (G)
7	20.75 (2 H)	3.32 (4 H)	20.75 (2 H)	2.0065	0.4
	20.70	4.10	20.70	2.0062	
8	20.90 (2 H)	3.24 (6 H)	20.90 (2 H)	2.0074	0.4
	20.85	4.06	20.85	2.0072	
9	20.80 (2 H)	3.10 (2 H)	20.80 (2 H)	2.0064	0.4
	20.80	3.60	20.80	2.0063	
10^b	4.95 (6 H)	0.25 (2 H)	7.40 (2 H)	2.0025	0.3

^a Photolysis of 3-alkylthiophenes and 4,4'-dialkyl-2,2'-bithiophenes in TFA. ^b Photolysis of 3,3'-dimethyl-2,2'-bithiophenes in TFA.

radical cations of both conformers in the range of −10 °C to 25 °C.



(7): R = C₂H₅; R' = H

(8): R = CH₃; R' = H

(9): R = cyclopentyl; R' = H

(10): R = H; R' = CH₃

The same spectra were obtained when dilute solutions of 3-butyl- and 3-heptylthiophene were irradiated under the same conditions in TFA giving the radical cations of the 4,4'-dialkyl-2,2'-bithiophenes in both conformations

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Table 7. UV-Visible Absorption Maxima of 2,2'-Bithiophenes in Cyclohexane and Trifluoroacetic Acid

	cyclohexane λ_{\max} (ϵ^a), nm	TFA, λ_{\max} , nm
7	306 (10500)	331, 422
8	307 (12300)	330, 422
9	309 (10500)	339, 426
10	244 (10700)	331, 397

^a ϵ : absorbance ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$).

which produced a quintet of quintets for every conformer. If the starting monomer was 3-methylthiophene or 4,4'-dimethyl-2,2'-bithiophene (**8**), an asymmetric spectrum, indicating the presence of two doublets, was observed which consisted of a quintet of septets for every conformer with the *h*s constants reported in Table 6. When irradiation in TFA solutions was performed on 3-cyclopentylthiophene or 4,4'-dicyclopentyl-2,2'-bithiophene (**9**), the same asymmetric spectrum was observed; a computer simulation also indicated that a mixture of two conformers corresponding to the radical cations of the dimer was obtained (Table 6).

When small quantities of thallium(III) trifluoroacetate were added to the above solutions, the hyperfine splitting of the spectra disappeared while a single and broad line corresponding to polymeric fractions was developed.

Thus, in all cases the radical cations of 3-alkylthiophenes, generated in the first stage of the oxidation in TFA, were too short-lived for EPR detection, and they rapidly dimerize. Radical cations of the dimers were relatively persistent, despite the fact that their most reactive positions for polymerization, C(5) and C(5'), are not blocked by alkyl groups. This persistence is mainly due to the very low concentrations of these radical species in TFA solution. As it was demonstrated for 2,2'-bithiophene and 2,2',5',2''-terthiophene, neutral dimers of these substituted bithiophenes are almost completely protonated in TFA medium, giving their conjugated acids. The UV-vis absorption maxima of them in cyclohexane and in TFA are given in Table 7. In all cases, a considerable bathochromic shift is observed going from the aprotic solvent to the acidic medium. Therefore, the concentration of the neutral species which are the active species to be oxidized by TFA is so low in this medium that their radical cations persist long enough to be detected before an oxidative coupling occurs. It is also noteworthy to point out, in relation to this persistence, the good properties of TFA in stabilizing radical cations due to its low nucleophilicity.

The oxidative dimerization of the radical cations of 3-alkylthiophenes mainly occurs at its less sterically hindered position. The radical cations of the isomeric dimers, 3,3'-dialkyl- and 3,4'-dialkyl-2,2'-bithiophenes, have not been observed by EPR, in spite of the fact that the doublet species of the first isomer has been independently generated from 3,3'-dimethyl-2,2'-bithiophene (**10**) and has proved to be stable enough in TFA (Figure 4). Concerning to this radical cation, the EPR spectrum of it shows a symmetric distribution of lines, with the coupling constants reported in Table 6, corresponding to one doublet species, which suggests the presence of only the *anti*-conformer, the *syn* being too unstable to be present due to the frontal repulsion between the methyl groups (Scheme 1).

From data in Table 6, two remarks deserve special comments: (1) the relative high-values of *g*-factors for the radical cations of 4,4'-dialkyl-2,2'-bithiophenes which

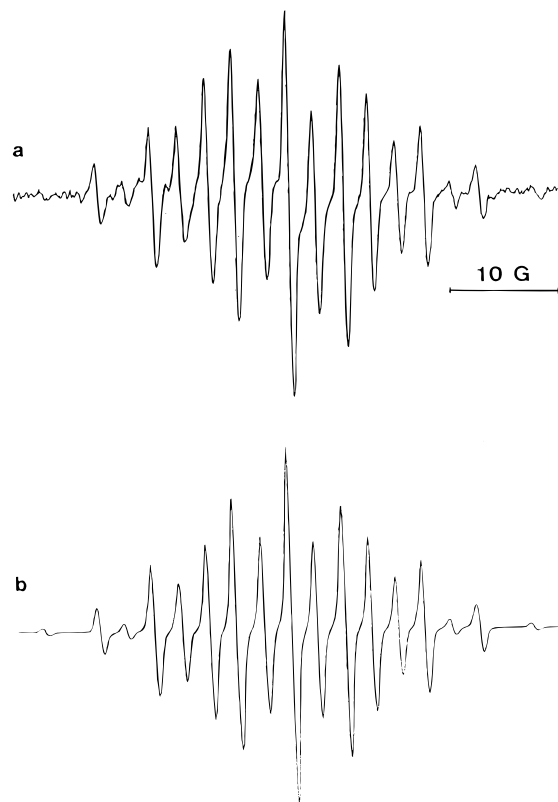
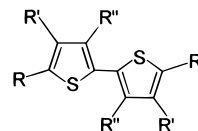


Figure 4. (a) EPR spectrum of an irradiated solution of 3,3'-dimethyl-2,2'-bithiophene (**10**) in trifluoroacetic acid at -10 °C. (b) Computer simulation using the parameters given in Table 7.

indicate stronger spin-orbit couplings with the sulfur atom in the molecule than the normal values for other isomers, and (2) the relative high spin-coupling constants with the four ring protons when disubstitution takes place in the 4,4'-positions. Concerning this, some preliminary results in the observation and detection by EPR of radical cations in tetrasubstituted 2,2'-bithiophenes indicate that when substitution takes place in 3,4,3',4'-positions, as in 3,4,3',4'-tetraethyl-2,2'-bithiophene (**11**) (Figure 5), the spectra are similar to those from 4,4'-dialkyl-2,2'-bithiophenes, with a high coupling constant for 5 and 5' ring-positions of ~ 20 – 23 G and a high *g*-value (2.0071). However when substitution is in 4,5,4',5'-positions, as in 4,5,4',5'-tetramethyl-2,2'-bithiophene (**12**) (Figure 6), the highest coupling constant for 5 and 5' ring-positions is ~ 9 G, and the *g*-value (2.0031) is closer to that of the free electron.



11: R=H; R'=R''=C₂H₅
12: R=R'=CH₃; R''=H

The rigidity observed by EPR spectroscopy in these 2,2'-bithiophenes, associated with a large barrier to rotate about C(2)–C(2') bond which results in the presence of both isomers, *syn* and *anti*, on the EPR timescale, is in agreement with MINDO/3 calculations carried out on the isomeric 5,5'-dialkyl-2,2'-bithiophenes.⁶ These estimations indicated the existence of large barriers to intramolecular rotation in radical cations and practically negligible barriers in the neutral compounds, as it was noted

Scheme 1

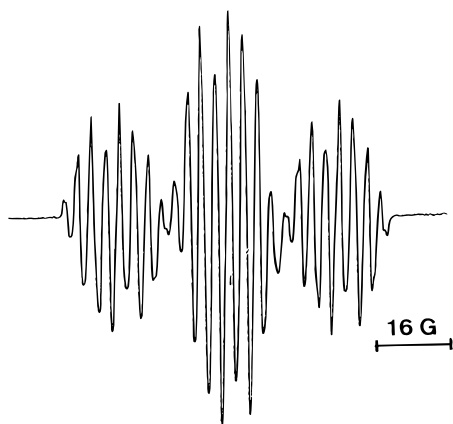
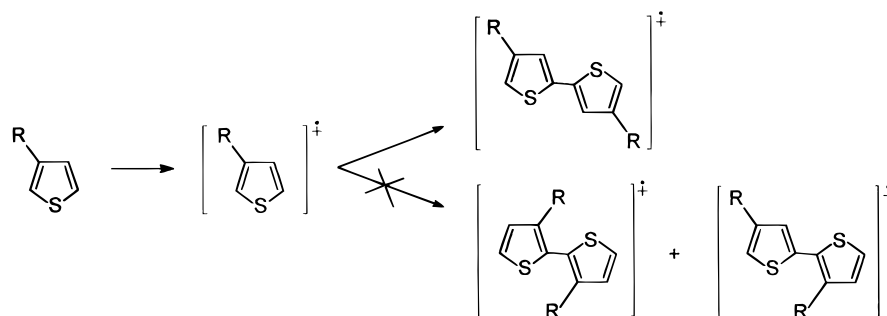


Figure 5. EPR spectrum of an irradiated solution of 3,4,4',5'-tetraethyl-2,2'-bithiophene in trifluoroacetic acid.

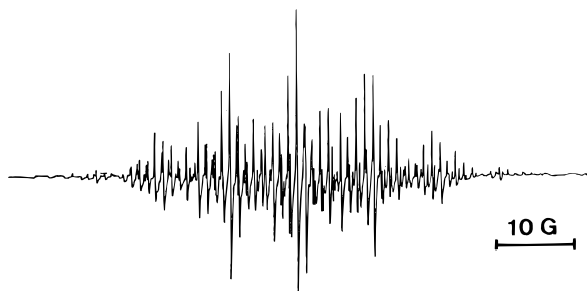


Figure 6. EPR spectrum of an irradiated solution of 4,5,4',5'-tetramethyl-2,2'-bithiophene in trifluoroacetic acid.

earlier by Alberti *et al.* applying the McLachlan procedure on short oligomeric thiophenes.¹⁴

Experimental Section

Melting points were obtained by using a Köfler microscope "Reichert" and are uncorrected. The IR spectra were recorded with a Perkin Elmer Model 683 spectrometer, and the UV-vis spectra with a Perkin Elmer Lambda Array 3840 spectrometer coupled with a Perkin Elmer 7300 computer. ¹H and ¹³C NMR spectra were determined at 200 MHz and 300 MHz with Varian Gemini 200 HC and XL-300 spectrometers, respectively. The electrical conductivities were determined on compressed pellets by van der Pauw's four-probe method.

The starting monomers, 3-ethylthiophene, 3-*n*-butylthiophene, and 3-*n*-heptylthiophene, were synthesized via the coupling of alkylmagnesium bromides with 3-bromothiophene in the presence of Ni(dppp)Cl₂ according to the method of Zimmer *et al.*¹⁵ and were distilled before use. 4,4'-Dimethyl-

2,2'-bithiophene (**8**)¹⁶ was synthesized from 3-methylthiophene, by lithiation with butyllithium followed by oxidative coupling with copper chloride.¹⁷ 3,3'-Dimethyl-2,2'-bithiophene (**10**)¹⁶ was prepared by iodination of 3-methylthiophene using the method of Suzuki *et al.*¹⁸ and reductive dimerization of the 2-iodo-3-methylthiophene according to the method of Iyoda *et al.*¹⁹ 4,5,4',5'-Tetramethyl-2,2'-bithiophene (**12**) was prepared by bromination of 3-methylthiophene, followed by methylation to 2,3-dimethylthiophene and oxidative dimerization according to the method of Gronowitz *et al.*²⁰ All these 2,2'-bithiophenes were identified by ¹H NMR spectra.

4,4'-Diethyl-2,2'-bithiophene (7). 7 was prepared according to a described procedure.¹⁷ A solution of *N,N,N,N*-tetramethylethylenediamine (12.05 mL; 40.3 mmol) and *n*-butyllithium (50.15 mL; 40.3 mmol) in ether (150 mL) was added dropwise to a stirred solution of 3-ethylthiophene (8.0 g; 36.0 mmol) in ether (250 mL) in inert (Ar) atmosphere and then refluxed (1 h). After cooling down to -78 °C, CuCl₂ (11.8 g, 49.0 mmol) was added, and the mixture was poured into an excess of diluted aqueous HCl and extracted with more ether. The organic layer, washed with water and dried over Na₂SO₄, was evaporated to give a residue which was chromatographed on column (silica gel, CCl₄) and then recrystallized from *n*-pentane at low temperature (-78 °C) to afford 4,4'-diethyl-2,2'-bithiophene (3.22 g; 40.5%): ¹H NMR (CDCl₃) δ 7.00 (d, 2H), 6.77 (d, 2H), 2.61 (q, 4H), 1.25 (t, 6H); ¹³C NMR (CDCl₃) (300 MHz) 145.3, 137.4, 124.5, 118.1, 23.6, 14.5. Anal. Calcd for C₁₂H₁₄S₂: C, 64.8; H, 6.3; S, 23.0. Found: C, 64.8; H, 6.2; S, 28.8.

2-Iodo-3,4-diethylthiophene. This thiophene was prepared according to a described procedure.¹⁸ A mixture of 3,4-diethylthiophene (1.0 g; 7.13 mmol), periodic acid (0.34 g; 1.5 mmol), and iodine (0.76 g; 3.0 mmol) in CH₃COOH-H₂O-H₂SO₄ (100:20:3) (40 mL) was magnetically stirred and warmed at 60–65 °C. After 4 h, the reaction mixture was poured into an excess of ice-water and extracted with ether. The organic layer was washed with an aqueous solution of NaHSO₃ and then with aqueous Na₂CO₃ and with water and evaporated at reduced pressure. Distillation of the residue (0.5 mmHg; 100 °C) gave 2-iodo-3,4-diethylthiophene (1.24 g; 65.2%): ¹H NMR (CDCl₃) δ 7.06 (s, 1H), 2.65–2.50 (m, 4H), 1.24 (t, 3H); ¹³C NMR (CDCl₃) (200 MHz) 146.8, 143.0, 124.7, 74.2, 23.9, 22.6, 13.9, 13.7, and the residue was 2,5-diiodo-3,4-diethylthiophene (0.37 g; 13.3%): mp 68–70 °C; ¹H NMR (CDCl₃) δ 2.62 (q, 8H, J = 7.6 Hz), 1.08 (t, 6H, J = 7.6 Hz); ¹³C NMR (CDCl₃) (200 MHz) 147.1, 77.3, 24.9, 14.4.

3,3,4,4'-Tetraethyl-2,2'-bithiophene (11). This bithiophene **11** was prepared according to a described procedure.²¹ A mixture of 2-iodo-3,4-diethylthiophene (1.0 g) and copper powder (2.56 g) was heated at 200 °C for 20 min. After cooling, the contents of the flask were extracted with hot CHCl₃. The organic solution was evaporated off and the residue in *n*-

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hexane was passed through a column (silica gel). The evaporation to dryness gave 3,4,3',4'-tetraethyl-2,2'-bithiophene (0.19 g; 36.5%): mp 30–2 °C (from methanol); ¹H NMR (300 MHz) (CDCl₃) δ 6.97 (d, 2H, *J*=1.2 Hz), 2.60 (qd, 4H, *J*=7.5 Hz, *J*'=1.2 Hz, 4,4' CH₂), 2.49 (q, 4H, *J*=7.5 Hz, 3,3' CH₂), 1.31 (t, 6H, *J*=7.5 Hz), 1.04 (t, 6H, *J*=7.5 Hz); ¹³C NMR (CDCl₃) 143.5, 142.6, 129.6, 119.6, 22.3, 20.6, 15.0, 13.6. Anal. Calcd for C₁₆H₂₂S₂: C, 69.0; H, 8.0; S, 23.0. Found: C, 69.1; H, 7.9; S, 23.0.

4,4'-Dicyclopentyl-2,2'-bithiophene (9). This bithiophene **9** was prepared according to a described procedure.¹⁷ A solution of *N,N,N,N*-tetramethylethylenediamine (0.62 mL; 4.2 mmol) and *n*-buthyllithium (1.6 mL; 2.5 M in hexane) in ether (7.5 mL) was added dropwise to a stirred solution of 3-cyclopentylthiophene (0.5 g; 3.28 mmol) in ether (12.5 mL) in an inert (Ar) atmosphere and then refluxed (1 h). After cooling down to –78 °C, CuCl₂ (0.6 g; 4.46 mmol) was added, and the mixture was stirred overnight at room temperature. The mixture was poured into an excess of diluted aqueous HCl and extracted with more ether. The organic layer, washed with water and dried over Na₂SO₄, was evaporated to give a residue which was chromatographed on column (silica gel, *n*-hexane) to afford 4,4'-dicyclopentyl-2,2'-bithiophene (0.117 g; 24%): mp 47–50 °C (from ethanol) ¹H NMR (CDCl₃) δ 7.01 (s, 2H), 6.79 (s, 2H), 3.00 (q, 2H), 2.06–2.00 (m, 4H), 1.79–1.56 (m, 12H); ¹³C NMR (CDCl₃) 148.1, 137.4, 124.0, 117.5, 41.4, 33.8, 25.1. Anal. Calcd for C₁₈H₂₂S₂: C, 71.5; H, 7.3; S, 21.2. Found: C, 71.5; H, 7.3; S, 20.8.

EPR Experiments. 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 a Hewlett-Packard 9835-B computer using a modified version of the software package of a Varian E-935 Data Acquisition System.

Spectra of polymeric samples were recorded at room temperature. To detect the radical cations of 2,2'-bithiophenes, solutions of the substrates, substituted thiophenes and 2,2'-bithiophenes, in TFA were degassed by passing a stream of dry argon through the solutions to remove oxygen, and then were photolyzed in the same cavity of the spectrometer at variable temperature using the light from an Oriel 500-W high pressure mercury arc.

Treatment of 3-Alkylthiophenes with Thallium(III) Trifluoroacetate (TTFA) in Trifluoroacetic Acid (TFA). General Procedure. A (1:1 molar proportion) solution of TTFA in TFA (30 mL) was added dropwise at room temperature to a stirred solution of monomer (0.5–1.5 g) in TFA (20 mL) in an inert (Ar) atmosphere. The mixture was stirred for another 1 h and then at reflux for additional time (24 h). The precipitate was separated by filtration, washed with TFA

and with an excess of water, and dried in a desiccator (18 h) and at reduced pressure (0.1 mmHg; 60 °C; 2 h).

From thiophene (3): 3 (1.03 g; 12 mmol) and TTFA (6.67 g; 12 mmol). A dark precipitate (0.65 g) was obtained. Analytical data are given in Table 1.

From 3-ethylthiophene (4): 4 (0.68 g; 6 mmol) and TTFA (3.3 g; 6 mmol). A dark precipitate (0.47 g) was obtained. Analytical data are given in Table 1.

From 3-*n*-buthylthiophene (5): 5 (0.57 g; 4 mmol) and TTFA (2.19 g; 4 mmol). A dark precipitate (0.31 g) was obtained. Analytical data are given in Table 1.

From 3-*n*-heptylthiophene (6): 6 (1.64 g; 9 mmol) and TTFA (4.96 g; 9 mmol). A dark precipitate (1.33 g) was obtained. Analytical data are given in Table 1.

Treatment of Polymeric Samples with Ethanol. General Procedure. The samples were purified by the use of a Soxhlet extractor with ethanol at reflux during 8 h. The soluble fractions gave, by evaporation to dryness, small residues: 3% from **3**, **4**, and **6**, and 4% from **5**. Analytical data of the residues from the four samples are given in Table 2.

From thiophene (3): IR (KBr) 3080 (vw), 1650 (s), 1525 (w), 1490 (m), 1415 (s), 1350 (m), 1280 (w), 1215 (m), 1170 (w), 1120 (m), 1035 (m), 825 (w), 780 (vs), 730 (w), 690 (m) cm⁻¹.

From 3-ethylthiophene (4): IR (KBr) 3060 (w), 2970 (s), 2940 (s), 2880 (m), 1780 (w), 1690 (s), 1515 (w), 1455 (s), 1370 (m), 1310 (w), 1250 (w), 1180 (m), 1045 (m), 1015 (w), 825 (vs), 770 (w) cm⁻¹.

From 3-*n*-buthylthiophene (5): IR (KBr) 3070 (w), 2965 (s), 2930 (s), 2865 (s), 1775 (w), 1690 (s), 1555 (w), 1510 (w), 1450 (s), 1375 (m), 1295 (w), 1245 (w), 1210 (w), 1170 (m), 1095 (m), 1070 (w), 925 (w), 890 (w), 820 (s), 785 (m), 735 (w), 715 (w) cm⁻¹.

From 3-*n*-heptylthiophene (6): IR (KBr) 3060 (vw), 2960 (s), 2920 (s), 2850 (s), 1690 (s), 1515 (w), 1455 (s), 1375 (m), 1340 (vw), 1190 (w), 1110 (w), 880 (vw), 820 (s), 715 (m) cm⁻¹.

Doping of Samples with I₂. General Procedure. The purified samples were exposed to I₂ vapors at atmospheric pressure and at room temperature (22 h) and then dried in vacuum (0.1 mmHg; 60 °C; 2 h). Analytical data of the iodided-samples are given in Table 3.

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