

Structure of the Radicals Formed in Thermal and Photochemical Reactions of 3-Alkylthiophenes under Acidic Conditions

Frederique Barbosa,^a Lennart Ebersson,^{b,*} Georg Gescheidt,^a Salo Gronowitz,^b
Anna-Britta Hörnfeldt,^b Luis Juliá^c and Ola Persson^b

^aInstitute of Physical Chemistry, University Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland, ^bDepartment of Chemistry, Lund University, PO Box 124, S-221 00 Lund, Sweden and ^cDepartament de Química Orgànica Biològica, CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain

Barbosa, F., Ebersson, L., Gescheidt, G., Gronowitz, S., Hörnfeldt, A.-B., Juliá, L., Persson, O., 1998. Structure of the Radicals Formed in Thermal and Photochemical Reactions of 3-Alkylthiophenes under Acidic Conditions. – Acta Chem. Scand. 52: 1275–1284. © Acta Chemica Scandinavica 1998.

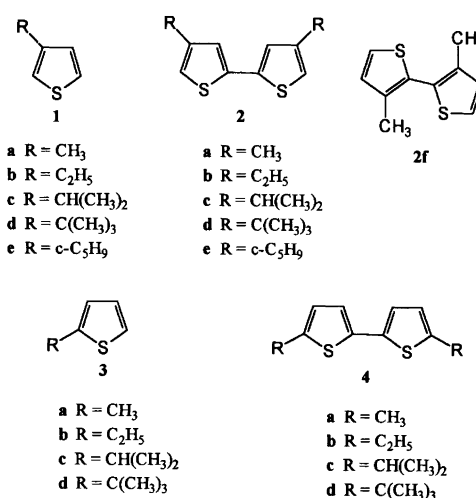
It is shown that thallium(III) tris(trifluoroacetate) (denoted Tl^{III}) in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) oxidizes 2-alkylthiophenes **3** to give the corresponding persistent 5,5'-dialkyl-2,2'-bithiophene radical cations, and that similar oxidation of 3-methylthiophene gives the EPR spectrum of the short-lived radical cation of 3,3'-dimethyl-2,2'-bithiophene.

The photolysis of 3-methylthiophene in HFP containing a small amount of methanesulfonic acid gave an EPR spectrum which was assigned the structure of the 5,5'-bisprotonated radical cation formally derived from the one-electron reduction of 5,5'-bis-protonated 4,4'-dimethyl-2,2'-bithiophene. Calculated (UB3LYP/6-31G**/UHF/3-21G*) EPR spectral parameters agreed well with this structure. Analogous species were detected from the thermal treatment of 3-ethyl-, 3-isopropyl- and 3-*tert*-butylthiophene by HFP–methanesulfonic acid. In HFP–sulfuric acid (0.7%) all four 3-alkylthiophenes gave these radicals in a thermal reaction.

The oxidation of 2,5-dimethylthiophene by Tl^{III} in HFP–trifluoroacetic acid (7%) gave solutions displaying EPR spectra which were assigned to *cis*- and *trans*-2,2',5,5'-tetramethyl-3,3'-bithiophene radical cations. Similar reactions occurred in HFP–sulfuric acid (0.7%).

Irradiation by UV light of a solution of a 3-alkylthiophene (**1a**, **b** and **e**) in trifluoroacetic acid leads to the development of EPR spectra of persistent species assigned to the *cis* and *trans* forms of the radical cation of the corresponding 5,5'-coupled bithiophene (**2^{•+}**).¹ More intense spectra were obtained from similar treatment of authentic samples of **2a**, **b** and **e**. It was earlier shown that 2-methylthiophene (**3a**) in dichloromethane–AlCl₃ at –80 °C gave rise to the EPR spectrum of two isomers of 5,5'-dimethyl-2,2'-bithiophene radical cation (**4a^{•+}**).²

However, the reported hfs constants (Fig. 1) of **2^{•+}** differed significantly from values expected from the EPR spectra of radical cations of other bithiophene derivatives.^{2–4} In particular, the identical large couplings, >2 mT, to the α and β hydrogens of **2^{•+}** are far from the typical values reported, 0.7–0.8 mT for α positions and 0.02–0.4 mT for β positions. The *g* values, 2.006–2.007, were larger than those found for radical



*To whom correspondence should be addressed.

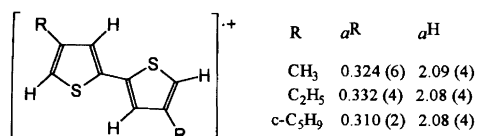


Fig. 1. Analysis and assignment of EPR spectra obtained by the UV irradiation of 4,4'-dialkyl-2,2'-bithiophenes **2** in TFA (Ref. 1).

cations of other bithiophenes, around 2.0026. Moreover, the relatively high persistency of these species, to be denoted $X^{\cdot+}$ in the following, is not in accordance with the high reactivities for further coupling of α positions of thiophene derivatives, leading to polymers.⁵

Analogous behaviour, i.e. formation of dimer type spectra with g values around 2.006 upon irradiation in trifluoroacetic acid, was earlier found for two 2,5-dialkylthiophenes (**5**), but a clearcut structural assignment of the spectra was not obvious.⁶

In view of these considerations, we have repeated and complemented some of this work by capitalizing on the much enhanced persistency of radical cations in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) and the sometimes better resolution obtained in this solvent.^{3,7} It is shown that thallium(III) tris(trifluoroacetate) (to be denoted Tl^{III} in the following) in HFP oxidizes 2-alkylthiophenes **3** to give the corresponding persistent 5,5'-dialkyl-2,2'-bithiophene radical cations $4^{\cdot+}$, and that Tl^{III} oxidation of 3-methylthiophene (**1a**) gives the EPR spectrum of the short-lived radical cation of 3,3'-dimethyl-2,2'-bithiophene ($2f^{\cdot+}$). The formation of species $X^{\cdot+}$ from the photolysis of 3-alkylthiophenes **1a–d** was found to depend on the acidity of the solution, and they were assigned the structure of the radical cation $2H_2^{\cdot+}$ formally derived from the one-electron reduction of 5,5'-bisprotonated **2**, $2H_2^{2+}$. In fact, species $X^{\cdot+}$ were formed from **1a–d** simply by thermal reactions in HFP-sulfuric acid (0.7%).

Cyclic voltammetry (CV) of 3-methylthiophene (1a) in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP). HFP has been shown to be a favourable solvent for the electrochemical study of radical cations and their polymerization by virtue of its ability to suppress strongly nucleophilic reactivity.⁸

CV of 3-methylthiophene **1a** in HFP-Bu₄NPF₆ at a sweep rate of 0.2 V s⁻¹ showed a chemically irreversible oxidation step at $E_{pa} = 1.49$ V vs. Ag/AgCl (an increment of 0.38 V should be added to obtain the potential in dichloromethane = 1.87 V). Repeated cycling at 0.1 V s⁻¹ led to the buildup of a dark deposit with the following electrochemical characteristics (Fig. 2a): the anodic E_{pa} moved about 0.1 V in the cathodic direction and shallow reduction peaks at $E_{pc} \approx 1.2$ and 0.6 V developed. An oxidation peak possibly matching the latter was seen at ca. 0.8 V, more pronounced at a sweep rate of 0.5 V s⁻¹ (Fig. 2b). The buildup of deposit became slower at higher sweep rates.

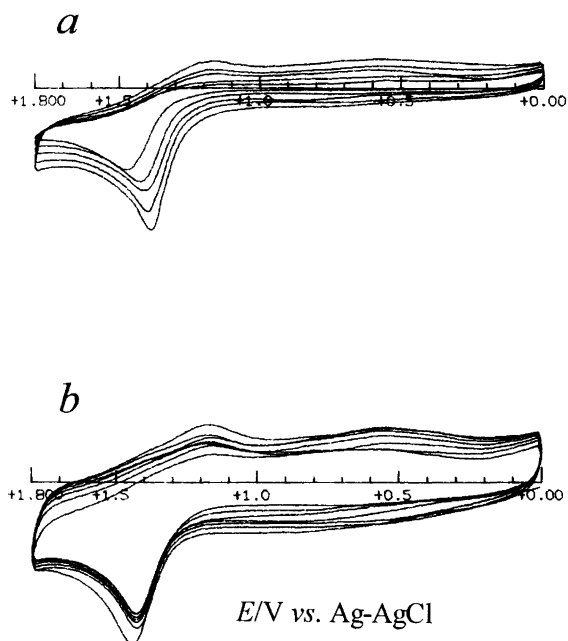


Fig. 2. Cyclic voltammetry of 3-methylthiophene (**1a**, 3 mmol dm⁻³) in HFP-Bu₄NPF₆ (0.15 mol dm⁻³) at (a) 0.1 and (b) 0.5 V s⁻¹.

*Cyclic voltammetry of 4,4'- (**2a**) or 5,5'-dimethyl-2,2'-bithiophene (**4a**) in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP).* CV of **2a** in HFP-Bu₄NPF₆ at a high sweep rate, 50 V s⁻¹, showed beginning chemical reversibility of the $2a^{\cdot+}$ -**2a** couple, E_{pa} and E_{pc} being 0.79 and 0.73 V, respectively (Fig. 3a). At 2 V s⁻¹, this couple was irreversible, with E_{pa} at 0.84 V, and two new chemically reversible couples built up at $E_{rev} = 0.62$ and 0.30 V (Fig. 3b). Thus even in HFP the radical cation $2a^{\cdot+}$ underwent rapid followup reactions, presumably with formation of oligomers of well defined composition. In dichloromethane, repetitive CV cycling of **2a** led to the expected buildup of a polymer (Fig. 3c).⁵

For the $4a^{\cdot+}$ -**4a** couple, the start of chemical reversibility was seen at a sweep rate of 0.1 V s⁻¹ ($E_{pa} = 0.77$ V and $E_{pc} = 0.68$ V, $E_{rev} = 0.72$ V), i_{pc}/i_{pa} reaching ca. 0.5 at 0.5 V s⁻¹. No sign of oligomer formation was noted upon repetitive scanning.

*EPR spectra from the oxidation of 2-alkylthiophenes (**3**) or 3-methylthiophene (**1a**) in HFP by Tl^{III}.* The addition of Tl^{III} to a solution of a 2-alkylthiophene (**3a**, **3b**, **3c** or **3d**) in HFP at 23 °C led to the development of EPR spectra of the corresponding 5,5'-dialkyl-2,2'-bithiophene radical cations ($4a^{\cdot+}$ - $4d^{\cdot+}$). In each case, two isomers were formed, and the spectra were similar to those reported earlier (Table 1), the g values being around 2.0025. These radical cations persisted for 5–10 h.

2-Isopropylthiophene **3c** was only available as a 63:37 mixture with its 3-isomer, but the latter had no effect on the EPR spectral behaviour under the conditions defined above. Similarly, 2-*tert*-butylthiophene **3d** had to be used as a 1:2 mixture with its 3-isomer, again with no effect

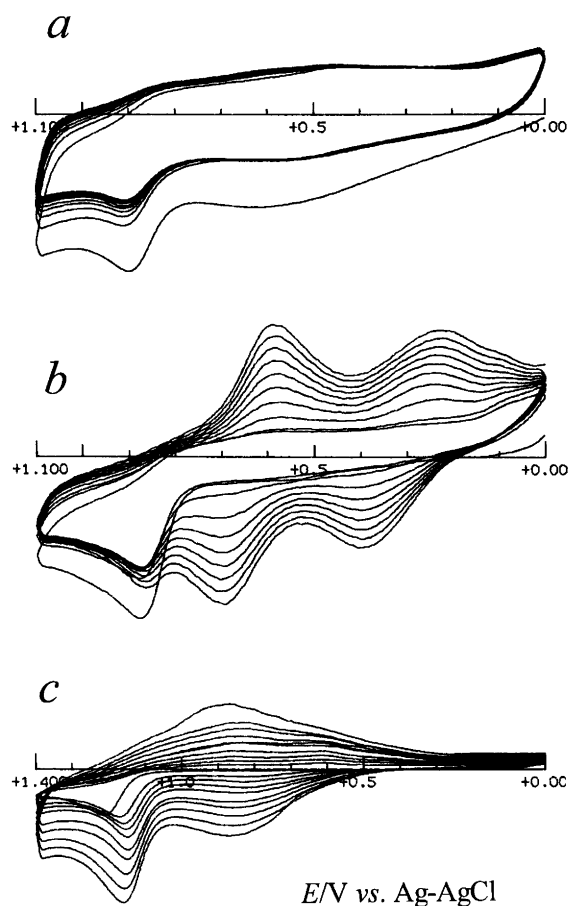


Fig. 3. Cyclic voltammetry of 4,4'-dimethyl-2,2'-bithiophene (**2a**, 1.3 mmol dm^{-3}) in HFP- Bu_4NPF_6 (0.15 mol dm^{-3}) at (a) 50 and (b) 0.5 V s^{-1} , or in (c) dichloromethane- Bu_4NPF_6 (0.15 mol dm^{-3}) at 2 V s^{-1} .

on the EPR spectral behaviour under the conditions defined above.

The addition of Ti^{III} to a solution of 3-methylthiophene (**1a**) in HFP-trifluoroacetic acid (3%) at 23°C led to the development of a weak EPR spectrum which was assigned the structure of the 3,3'-dimethyl-2,2'-bithiophene radical cation ($\mathbf{2f}^+$) on the basis of its hfs constants, $a^{\text{CH}_3} = 0.489$ (6 H), $a^{\text{H}^5, \text{H}^5'} = 0.729$ (2 H) and $a^{\text{H}^4, \text{H}^4'} = 0.023$ (2 H) mT and its g value = 2.0026. The radical cation of authentic 3,3'-dimethyl-2,2'-bithiophene **2f** has been generated in trifluoroacetic acid,¹ and its EPR spectrum had $a^{\text{H}^5, \text{H}^5'} = 0.74$ (2 H), $a^{\text{H}^4, \text{H}^4'} = 0.023$ (2 H) and $a^{\text{CH}_3} = 0.495$ (6 H) mT, with a g value of 2.0025. The EPR spectrum of $\mathbf{2f}^+$ disappeared within ca. 20 min, in line with the behaviour of the even more shortlived 2,2'-bithiophene radical cation in HFP [$a^{\text{H}^5, \text{H}^5'} = 0.77$ (2 H), $a^{\text{H}^4, \text{H}^4'} = 0.027$ (2 H) and $a^{\text{H}^3, \text{H}^3'} = 0.385$ (2 H) mT].³

Neither 3-ethylthiophene **3b** nor 3-isopropylthiophene **3c** gave any significant paramagnetic activity upon similar treatment with Ti^{III} . The solutions rapidly became black, presumably due to formation of polymers, and featured a weak undefined signal centered at $g \approx 2.005$.

EPR spectra of 3-methylthiophene (**1a**) or 4,4'-dimethyl-2,2'-bithiophene (**2a**) in HFP with small amounts of acid present under photochemical conditions. The irradiation of 3-methylthiophene **1a** in trifluoroacetic acid by UV light led to the development of spectra of X^+ provided the concentration of **1a** was not too low. No spectrum was seen at $[\mathbf{1a}] = 30 \text{ mmol dm}^{-3}$, whereas at 150 mmol dm^{-3} the spectrum developed within 20 min. We suspected that the protonated form of **1a**, $\mathbf{1aH}^+$, might play a role in the mechanism leading to X^+ , and therefore repeated the photochemical reaction in HFP with a small amount of a protic acid present. With trifluoroacetic acid (5%) present no EPR spectrum was obtained, whereas addition of methanesulfonic acid (3%) caused an intense spectrum of X^+ to appear. It had the same gross features as those reported with neat trifluoroacetic acid as the solvent, but with an additional small coupling to two hydrogens resolved. Two similar spectra in a ratio of 4:1 were characterized: Major form: $g = 2.0068$, $a^{\text{H}} = 2.044$ (4), 0.395 (6) and 0.033 (2) mT; minor form: $g = 2.0070$, $a^{\text{H}} = 2.015$ (4), 0.319 (6) and 0.023 (2) mT (Table 2).

Irradiation of the yellow-green solution of authentic **2a** in HFP- $\text{CH}_3\text{SO}_3\text{H}$ (1.5%) gave rise to an intense EPR spectrum of X^+ with the same EPR spectral parameters as above. The spectrum obtained by irradiation of **2a** in HFP-trifluoroacetic acid (8%) was nearly identical.

With sulfuric acid (0.7%) as the acid, 3-methylthiophene gave a spectrum of X^+ already under thermal conditions (Table 2). It persisted for 2–3 h. Irradiation of 3-methylthiophene in (O - ^2H)HFP with ($^2\text{H}_2$)sulfuric acid present or in (^2H)trifluoroacetic acid gave an EPR spectrum which agreed well with that expected for a species where the groups of four and two hydrogens had been replaced by deuterium (Table 2). Weaker spectra (ca. 40%) of two forms of a species where only three of the 2.04 mT hydrogens had been exchanged were also detectable (see below). In (^2H)TFA under photolysis conditions, 4,4'-dialkyl-2,2'-bithiophenes **2a** and **2b** gave EPR spectra of X^+ in which all four hydrogens were exchanged for deuterium.

On the other hand, thermal treatment of a saturated solution of **2a** in HFP-sulfuric acid or (O - ^2H)HFP- ($^2\text{H}_2$)sulfuric acid did not produce any spectrum, whereas UV irradiation of these solutions gave a weak spectrum of X^+ or ($^2\text{H}_6$) X^+ [together with ($^2\text{H}_5$) X^+].

EPR spectrum from the oxidation of 4,4'-dimethyl-2,2'-bithiophene (**2a**) in HFP by 4-tolyl- Ti^{III} bis(trifluoroacetate). 4-Tolyl- Ti^{III} bis(trifluoroacetate), to be denoted tolyl- Ti^{III} in the following, is a less reactive alternative to Ti^{III} capable of oxidizing compounds with $E^\circ_{\text{rev}} < 1.5 \text{ V}$ vs. Ag/AgCl (valid in dichloromethane; in HFP, the corresponding limiting value is 1.1 V vs. Ag/AgCl). In neat HFP, tolyl- Ti^{III} immediately oxidized **2a** to blue-black species with insignificant paramagnetic activity, showing that $\mathbf{2a}^+$ is highly reactive toward an excess of

Table 1. EPR spectra of 5,5'-dialkyl-2,2'-bithiophenes or 4,4'-dimethyl-2,2'-bithiophene obtained by the oxidation of 2-alkylthiophenes or 3-methylthiophene (multiplicity given in parentheses); in this work the following concentrations were used: [substrate] $\approx 0.1 \text{ mol dm}^{-3}$, $[\text{Tl}^{\text{III}}] \approx 0.01 \text{ mol dm}^{-3}$.

Substituent in thiophene	Conditions (oxidant, solvent, temperature)	a^{H}/mT	a^{H}/mT	a^{R}/mT	g	Ratio (upper: lower)
2-Me	Tl ^{III} in HFP at 23 °C	0.091 (2)	0.383 (2)	0.879 (6)	2.0026	1.5
		0.065 (2)	0.405 (2)	0.894 (6)	2.0026	
2-Me	DCM–AlCl ₃ at –80 °C (Ref. 2)	0.094 (2)	0.391 (2)	0.908 (6)	2.00285	2
		0.070 (2)	0.412 (2)	0.924 (6)	2.00281	
2-Me	TFA–H ₂ SO ₄ at 17 °C (Ref. 14b)	0.091 (2)	0.382 (2)	0.875 (6)	2.0022	
		0.064 (2)	0.405 (2)	0.893 (6)	2.0022	
2-Et	Tl ^{III} in HFP at 23 °C	0.095 (2)	0.390 (2)	0.889 (4)	2.0026	0.33
		0.068 (2)	0.397 (2)	0.892 (4)	2.0026	
2-iPr ^a	Tl ^{III} in HFP at 23 °C	0.078 (2)	0.378 (2)	0.762 (2) 0.024 (12)	2.0031	Not possible to see
2-iPr	<i>hν</i> of TFA–Hg(OCOCF ₃) ₂ at –10 °C (Ref. 2)	0.075 (2)	0.382 (2)	0.752 (2)	2.00275	1.5
				0.025 (12)		
		0.078 (2)	0.377 (2)	0.768 (2) 0.026 (12)	2.00266	
2- <i>tert</i> -Bu ^b	Tl ^{III} in HFP at 23 °C	0.099 (2)	0.435 (2)	0.033 (18)	2.0023	1.3
		0.102 (2)		0.034 (18)	2.0023	
2- <i>tert</i> -Bu	DCM–AlCl ₃ at 10 °C (Ref. 2)	0.105 (2)	0.413 (2)	0.035 (18)	2.00265	1.3
		0.108 (2)	0.403 (2)	0.036 (18)	2.00262	
3-Me (1a)	Tl ^{III} in HFP–TFA (3%) at 23 °C	0.023 (2)	0.729 (2)	0.489 (6)	2.0023	
3-Et (1b)	Tl ^{III} in HFP–TFA (3%) or HFP at 23 °C	No spectrum				

^aA mixture of 2- and 3-isomer (63:37) was used. ^bA mixture of 2- and 3-isomer (37:63) was used.

2a, as suggested by the CV experiments of Fig. 2. In order possibly to block further reaction of **2a**^{•+}, some trifluoroacetic acid (3%) was added to protonate **2a**, and thus lower its concentration. This led to the development of a weak EPR spectrum with $g=2.0026$ and hfs constants of $a^{\text{H}}=0.78$ (2 H), 0.326 (2 H) and 0.094 (2 H) mT detectable above the noise level.

*EPR spectra of 3-ethylthiophene (1b), 3-isopropylthiophene (1c) and 3-*tert*-butylthiophene (1d) in HFP with a small amount of acid present under thermal conditions.* The mere standing of solutions of either of **1b**, **1c** or **1d** in HFP–methanesulfonic acid (3%) led to the development of weak spectra of X^{•+} (Table 2). In each case mixtures of two isomers were detected, and the small coupling constant to a group of two hydrogens was evident in all spectra. Irradiation by UV light caused the spectra to decrease in intensity. With sulfuric acid (0.15–0.7%) as the acidic component, the spectra were more intense.

3-*tert*-Butylthiophene **1d** was only available as a 2:1 mixture with its 2-isomer, but the latter had no effect on the EPR spectral behaviour of **1d** under thermal acidic conditions.

Treatment of 3-methyl- (**1a**), 3-ethyl- (**1b**), 3-isopropyl- (**1c**) or 3-*tert*-butylthiophene (**1d**) by (²H₂)sulfuric acid

in (*O*-²H)-HFP gave an EPR spectrum which agreed well with the one expected for a species where the groups of four and two hydrogens had been replaced by deuterium (Table 2). The simplicity of the spectrum derived from **1d** allowed for the ready detection of a less intense (ca. 40%), second pair of spectra which featured one remaining 2.04 mT coupling in addition to the 0.31 mT coupling to three deuterium atoms. Once this had been established, weaker spectra of the same appearance were detectable in the more complex spectra of **1a–1c**. The spectrum derived from 3-isopropylthiophene is shown in Fig. 4, together with a simulation of a superposition of the four spectra.

Cyclic voltammetry of 2,5-dimethylthiophene (5a) in HFP.

CV of **5a** in HFP–Bu₄NPF₆ at 50 V s^{–1} demonstrated the beginning of chemical reversibility, E_{pa} and E_{pc} being 1.34 and 1.18 V, respectively, and thus $E_{\text{rev}}=1.26$ V. At 0.1 V s^{–1}, repeated cycling showed that the second positive scan featured a new peak at $E_{\text{pa}}=0.97$ V, also seen in subsequent scans. No matching reduction peak was seen.

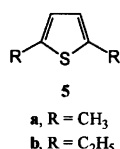
EPR spectral behaviour of 2,5-dimethylthiophene (5a) under different conditions.

As reported earlier,⁶ the UV irradiation of **5a** under acidic conditions, here HFP–methanesulfonic acid (1%), gave a septet of septets

Table 2. EPR spectra of $X^{\cdot+}$ obtained by the photochemical or thermal treatment of 3-alkylthiophenes **1** under acidic conditions at 23 °C (multiplicity given in parentheses); [substrate] 0.1–0.2 mol dm⁻³.

R group	Conditions	a^H/mT	$a^{H'}/mT$	a^R/mT	g	Ratio upper: lower
3-CH ₃ 1a	HFP–MeSO ₃ H (3%) $h\nu^a$	0.033 (2) 0.023 (2)	2.044 (4) 2.015 (4)	0.395 (6) 0.319 (6)	2.0068 2.0070	4
3-CH ₃ 1a	HFP–H ₂ SO ₄ (0.7%) thermal	0.034 (2) 0.023 (2)	2.050 (4) 2.043 (4)	0.400 (6) 0.314 (6)	2.0068 2.0070	1
3-CH ₃ 1a	(<i>O</i> - ² H)HFP–(² H ₂)H ₂ SO ₄ (0.15%) thermal	<0.005 <0.005	0.313 (4 ² H) 0.310 (4 ² H)	0.395 (6) 0.319 (6)	2.0068 2.0070	0.9 ^b
3-CH ₃ 1a	TFA neat, $h\nu$ (Ref. 1)	— —	2.085 (4) 2.090 (4)	0.406 (6) 0.324 (6)	2.0072 2.0074	
3-C ₂ H ₅ 1b	HFP–MeSO ₃ H (3%) thermal	0.034 (2) 0.020 (2)	2.031 (4) 2.015 (4)	0.390 (4) 0.319 (4)	2.0068 2.0070	3–4
3-C ₂ H ₅ 1b	HFP–H ₂ SO ₄ (0.7%) thermal	0.033 (2) 0.022 (2)	2.042 (4) 2.030 (4)	0.389 (4) 0.314 (4)	2.0068 2.0070	2
3-C ₂ H ₅ 1b	(<i>O</i> - ² H)HFP–(² H ₂)H ₂ SO ₄ (0.15%) thermal	<0.005 <0.005	0.311 (4 ² H) 0.309 (4 ² H)	0.393 (4) 0.314 (4)	2.0068 2.0070	2 ^b
3-C ₂ H ₅ 1b	TFA neat, $h\nu$ (Ref. 1)	— —	2.070 (4) 2.075 (4)	0.410 (4) 0.332 (4)	2.0062 2.0065	
3-CH(CH ₃) ₂ 1c	HFP–MeSO ₃ H (3%) thermal	0.032 (2) 0.021 (2)	2.042 (4) 2.031 (4)	0.283 (2) 0.240 (2)	2.0068 2.0070	0.8
3-CH(CH ₃) ₂ 1c	(<i>O</i> - ² H)HFP–(² H ₂)H ₂ SO ₄ (0.7%) thermal	<0.005 <0.005	0.310 (4 ² H) 0.310 (4 ² H)	0.283 (2) 0.240 (2)	2.0068 2.0070	0.8 ^b
3-C(CH ₃) ₃ 1d	HFP–MeSO ₃ H (3%) thermal	0.031 (2) 0.021 (2)	2.06 (4) 2.05 (4)	— —	2.0070 2.0072	0.5
3-C(CH ₃) ₃ 1d	HFP–H ₂ SO ₄ H (0.7%) thermal	0.030 (2) 0.020 (2)	2.03 (4) 2.04 (4)	— —	2.0070 2.0072	0.8
3-C(CH ₃) ₃ 1d	(<i>O</i> - ² H)HFP–(² H ₂)H ₂ SO ₄ (0.7%) thermal	<0.005 <0.005	0.312 (4 ² H) 0.312 (4 ² H)	— —	2.0070 2.0072	0.8 ^b

^aBefore irradiation, only a weak spectrum was detected. ^bAlso two spectra of the forms with one 2.04 mT proton left were seen. They had the same g values and their intensities were ca. 40% of each of the two other spectra. See also Fig. 4.



centered at $g=2.0067$, a^H 0.486 (6 H) and 0.216 (6 H) mT, reported⁶ in trifluoroacetic acid: $g=2.0064$, a^H 0.49 (6 H) and 0.21 (6 H) mT.

Oxidation of **5a** by tolyl-Tl^{III} in HFP gave the same spectrum, but with indications of a second spectrum at a lower g . Oxidation of **5a** by Tl^{III} in HFP–trifluoroacetic acid (7%) gave an EPR spectrum of two components in a ratio of ca. 0.6:1, the former one identical to the major spectrum above (Fig. 5). The latter spectrum had $g=2.0037$ and a^H 0.76 (6 H), 0.419 (6 H) and 0.034 (2 H) mT.

Discussion

General. The oxidation of aromatic compounds to their radical cations by Brønsted acids, either thermally or

photochemically, is a well established phenomenon which most recently was treated by Rathore and Kochi.⁹ Convincing evidence was given that the thermal oxidation of a redox reactive substrate, like octamethylbiphenylene or tetra(4-anisyl)ethylene, in dichloromethane containing methanesulfonic or tetrafluoroboric acid proceeds according to the protonation–electron transfer sequence shown in eqns. (1)–(4). In this mechanism, the initial protonation of the donor substrate **D** gives an oxidizing species DH^+ , which will oxidize **D** to $D^{\cdot+}$. The fate of the neutral species DH^{\cdot} was assumed to be further protonation–reduction to ultimately give DH_2 on the basis of the overall stoichiometry.



Depending on the strength of the acid, the redox potential of the substrate and the stability of the radical cation this scheme often will lead to a detectable concen-

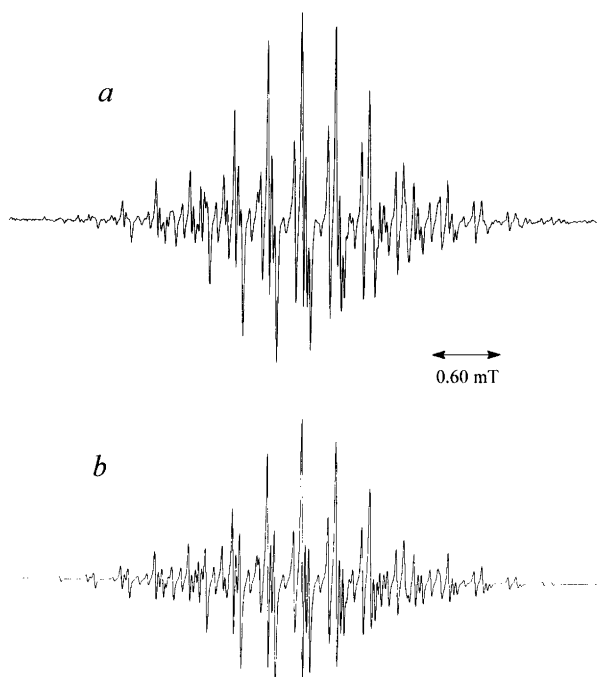


Fig. 4. (a) EPR spectrum of 3-isopropylthiophene (**1c**) (0.2 mol dm^{-3}) in ($O\text{-}^2\text{H}$)HFP-($^2\text{H}_2$) H_2SO_4 (0.7%) and (b) a simulation based on the parameters given in Table 2, two spectra representing species deuteriated in a 2+4 fashion, and two spectra representing deuteriation in a 2+3 fashion, ratio 1:1.25:0.4:0.5.

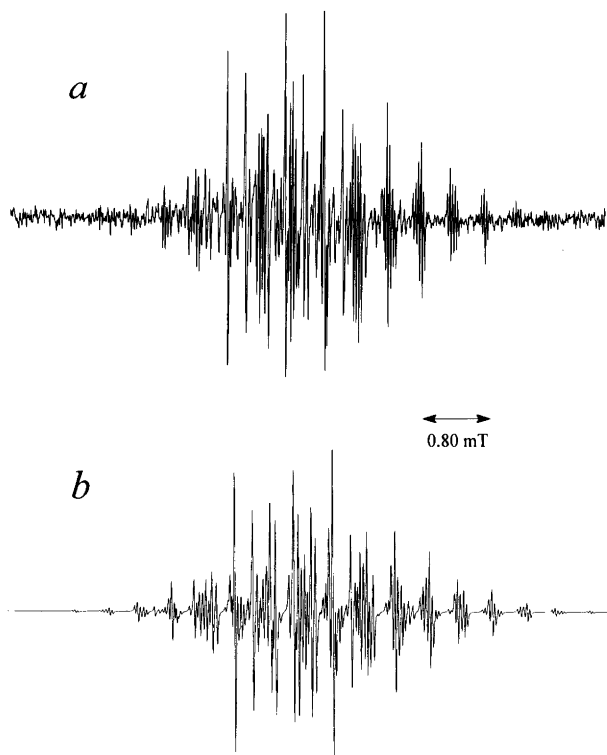
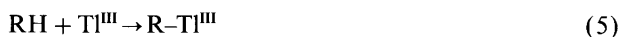


Fig. 5. EPR spectrum of (a) a solution of 2,5-dimethylthiophene (0.11 mol dm^{-3}) and Ti^{III} (ca. 0.01 mol dm^{-3}) in HFP at room temperature, and (b) a simulation based on the spectral parameters given in the text, ratio 0.6:1.

tration of D^+ under thermal or photochemical conditions, and this method of generation has therefore been much employed in EPR spectral studies. Trifluoroacetic acid, which combines Brønsted acidity with favourable properties in the stabilization of radical cations, has been an often used solvent. Thus the oxidation reactions feasible in the presence of Brønsted acids are readily understandable, even if it is difficult to pinpoint exact mechanisms in each individual case. However, the role of acid can also be to induce electrophilic oligomerization reactions, known to occur with thiophenes.¹⁰

The oxidation of aromatic compounds by Ti^{III} or tolyl- Ti^{III} is an excellent method to prepare solutions of radical cations for EPR spectroscopy,¹¹ especially in HFP or HFP containing small amounts of trifluoroacetic acid in order to enhance the concentration of the active Ti^{III} species.³ The advantage of the method depends largely on a mechanistic feature: the reaction takes place via an initial thallation step, and the organothallium species then somehow slowly decomposes to produce a low, but persistent concentration of the radical cation. This is a favourable situation for recording EPR spectra, as compared to the situation when a 'one-shot' strong ET oxidant is used.^{7,12} The details of the mechanism are not clear, but may for example involve the steps of eqns. (5)–(7).



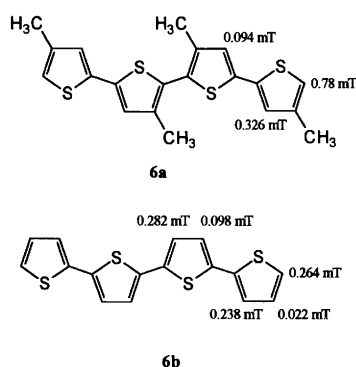
The disadvantage of using Ti^{III} is its tendency to promote biarene coupling, but this side-reaction can sometimes be avoided by using the less reactive 4-tolyl- Ti^{III} reagent. Depending on the kinetic properties of the participating species, both monomeric and dimeric radical cations can be observed in succession or sometimes only the dimeric one. It is possible that the mechanism of eqns. (5)–(7) has some direct connection to the dimerization process.¹³

Oxidation of 2-alkylthiophenes (4) and 3-methylthiophene (1a) by Ti^{III} in HFP under non-acidic conditions. 2-Alkylthiophenes (**3a–3d**) upon oxidation by Ti^{III} in HFP gave persistent EPR spectra of the corresponding 5,5'-dialkyl-2,2'-bithiophenes, **4a–4d**, the parameters of which agreed well with published values (Table 1). These spectra had g values around 2.0025, as commonly found for bithiophene EPR spectra. No sign of the monomeric radical cations were seen, in line with the high reactivity of the 5-position in $\mathbf{3}^{\cdot+}$. The electrochemical properties of one of the dehydrodimers, **4a**, in HFP agreed well with the persistency of its radical cation, previously described as being 'extremely unstable' in acetonitrile.^{14a}

One of the 3-alkylthiophenes, **1a**, upon similar oxidation gave rise to an EPR spectrum which was derived from the 3,3'-dimethyl-2,2'-bithiophene radical cation $\mathbf{2f}^{\cdot+}$. The g value was 2.0026, and the radical had

essentially disappeared within 20 min. Again, this behaviour is in line with the expected one: the 5- and 2-positions of $1a^{\cdot+}$ are reactive and rapid dimerization to $2a^{\cdot+}$ and/or $2f^{\cdot+}$ (and/or perhaps even a mixed dimer) occurs. These radical cations have open α -positions and thus can undergo fast followup reactions with eventual formation of oligomers-polymers, as indicated in the CV experiments. The fact that only $2f^{\cdot+}$ was detected by EPR spectroscopy is presumably due to a complex interplay of kinetic factors.

The oxidation of authentic $2a$ by tolyl-TI^{III} in HFP-trifluoroacetic acid (3%) gave a low concentration of a species displaying an EPR spectrum with a discernible 3×3 line pattern, $a^H = 0.78$ (2 H), 0.326 (2 H) and 0.094 (2 H) mT, clearly different from the spectrum assigned to $2a^{\cdot+}$ above. Tentatively, we may assign this spectrum to a radical cation of quaterthiophene structure $6a$, formally formed by coupling of $2a^{\cdot+}$ via the 5-positions, even if the agreement with the published hfs constants of the parent radical cation of $6b^{15}$ is not good.



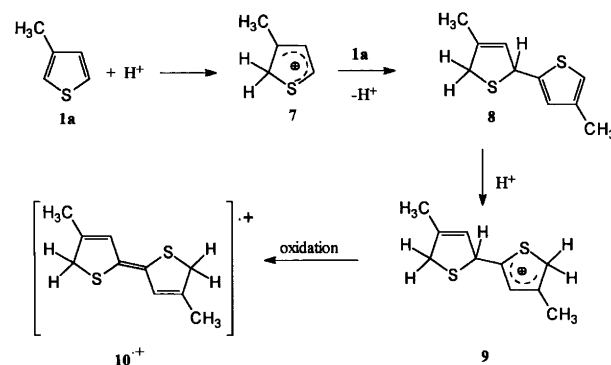
Cyclic voltammetry of 3-methylthiophene ($1a$) in HFP showed that $1a$ was oxidized at $E_{pa} = 1.49$ V with the buildup of a deposit with rather undefined characteristics (Fig. 2). There was an indication of a shallow oxidation peak around 0.8 V, the position expected for oxidation of any $2a$ or $2f$ formed. The anodic oxidation of $2a$ showed initial chemical reversibility with $E_{rev} = 0.76$ V at a sweep rate of 50 V s^{-1} . A comparison with the CV behaviour of other radical cations in HFP, for example (dibenzothiophene) $^{\cdot+}$,^{3b} suggests that EPR spectral observation of $2^{\cdot+}$ by the TI^{III} oxidation mechanism should just be feasible. At lower sweep rates, well defined chemically reversible couples at $E_{rev} = 0.62$ and 0.30 V appeared, whereas in dichloromethane a polymer was formed. This attests to the favourable properties of HFP as a solvent for studying electropolymerization (Fig. 1).⁸

Irradiation or thermal treatment of 3-methylthiophene ($1a$) or 4,4'-dimethyl-2,2'-bithiophene ($2a$) under acidic conditions in HFP. Since the initial experiments with UV irradiation of 3-methylthiophene ($1a$) in trifluoroacetic acid or HFP with trifluoroacetic acid present indicated that protonation was essential for the development of the EPR spectrum of species $Xa^{\cdot+}$, the photochemical

experiments of $1a$ or $2a$ were instead conducted in the presence of small amounts of methanesulfonic acid, the acid employed by Rathore and Kochi.⁹ Intense spectra of two isomers of $Xa^{\cdot+}$ were obtained, and the excellent resolution obtainable in HFP revealed a third coupling constant to a group of two protons. With sulfuric acid, the same spectrum was obtained from $1a$ in a thermal reaction, but not from $2a$, which gave a weak spectrum of $Xa^{\cdot+}$ only upon irradiation.

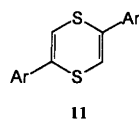
As noted above, the appearance of a group of four identical protons with a coupling constant > 2.0 mT in the EPR spectrum of $Xa^{\cdot+}$ in addition to a significantly larger g value of 2.007 is not compatible with EPR spectra of other 2,2'-bithiophenes known so far. We suggest an alternative assignment of these spectra to dimeric radical cation $10^{\cdot+}$, formally and perhaps also actually derived from $1a$ as shown in Scheme 1. Protonation of $1a$ at the 2-position¹⁰ would lead to 7 , which attacks the 2-position of a second molecule of $1a$ to give 8 . Protonation of 8 and further oxidation of 9 with loss of a proton, either thermally or photochemically, would eventually give $10^{\cdot+}$, a species with the expected EPR spectral characteristics of $Xa^{\cdot+}$. In $10^{\cdot+}$ the aromatic character of the thiophene system is abolished, and what results is formally the radical cation of a 1,3,6-triene system with two 3,4-*S*-alkyl and two 1,6-dimethyl groups. This species can exist as *cis* and *trans* forms. The pattern of three groups of six, four and two equivalent hydrogens fits with the EPR spectral results, and the higher g value is in agreement with those of similar sulfur radical cations, like those of 2,5-diaryldithiins ($11^{\cdot+}$, $g = 2.009$ in HFP).¹⁶

We stress that Scheme 1 does not represent the only mechanism possible for the formation of $10^{\cdot+}$ from $1a$; a number of other reaction sequences involving protonated species and radical cations along the lines of eqns. (1)–(4) can be formulated, and it is not possible to give preference to any particular mechanism at present stage. This is also indicated by its ready formation by irradiation of $2a$ under acidic conditions but not thermally. Compound $2a$ is easily protonated¹ to $2a-H^+$. Excitation of this intermediate will give $(2a-H^+)^*$ which is much more basic than $2a-H^+$ and thus can be further



Scheme 1.

protonated¹⁷ to give **2a**-H₂²⁺; reduction of the latter will give **10**^{•+}.



The other 3-alkylthiophenes, **3b-d**, did not require irradiation for EPR spectra of **Xb-d**^{•+} to develop. In these cases, sulfuric acid (0.15–0.7%) in HFP gave stronger signals than methanesulfonic acid. These spectra are assigned structures analogous to **10**^{•+}. Spectra recorded in suitably deuteriated media showed that the hydrogens attached to the former thiophene rings were exchanged toward deuterium, but also spectra from species with one of the 2.0 mT hydrogens intact were seen. It is not clear if the appearance of these spectra has any mechanistic connotation or if it only reflects slow H-²H exchange rates of intermediates/products involved. However, experiments carried out in trifluoroacetic acid show different behaviour starting from 3-methylthiophene or 4,4'-dimethyl-2,2'-bithiophene. With the monomer, a dimeric species with one of the 2.0 mT hydrogen intact was seen, and with the dimer, only the species with all four 2.0 mT hydrogens exchanged was detected.

Calculation of hfs constants of the radical cations 2a^{•+}, 2f^{•+} and 10^{•+}. Hfs constants were calculated by the UB3LYP/6-31G**/UHF/3-21G* method¹⁸ for *cis* and *trans* isomers of the new radical cation **10**^{•+} (Table 3). For comparison, similar calculations were performed for **2a**^{•+} and **2f**^{•+}, the former being included to ensure that the calculated hfs constants of **2a**^{•+} are sufficiently different from those of **10**^{•+}. Indeed they are, and this is important to establish since the EPR spectrum of **2a**^{•+} could not be recorded. The spectrum of one of the forms of **2f**^{•+} is known¹ and well reproduced by the calculations (Table 3). In view of the calculated energy difference between the *trans* and *cis* forms, 6.5 kcal mol⁻¹, it is understandable why only one form is observed by EPR spectroscopy.

The calculated hfs constants for the *trans* or *cis* isomer of **10**^{•+} are nearly the same and cannot be used for an

assignment to either of the experimental spectra. In Table 3 the assignment is based on the higher proportion of one of the isomers (ratio 4:1) observed in HFP-MeSO₃H (3%), in combination with the lower energy calculated for *trans*-**10**^{•+}. Since the isomer ratio is different under other conditions (Table 2), this assignment is still uncertain. However, the important feature is that the agreement between calculated and experimental values is excellent for both forms, providing strong support for the structure of **10**^{•+} as the genesis of the EPR spectra observed. Also, the conformer of **10**^{•+} with perpendicular rings is about 19 kcal mol⁻¹ higher in energy than either of the *cis* or *trans* isomer. Assuming that this is a good representation of the transition state, the existence of two rather stable isomers, detectable on the EPR timescale, is explicable in the same way for other bithiophene-type radical cations.²

Comment on the use of 2-/3-isomer mixtures. Since 3-*tert*-butylthiophene was only available in admixture with the 2-isomer (ratio 3-:2- = 63:37) some comment is required as to whether it is appropriate to use this mixture in the experiments reported above. We checked this aspect by using a separately prepared 2-/3-isomer mixture of 2-isopropylthiophene (ratio 2-:3- = 63:37) in the same experimental setup and found that it gave the same results as a sample of 3-isopropylthiophene free from the 2-isomer. Thus the 2-isomer does not interfere with experiments aiming at exploring the reactivity of the 3-isomer under acidic conditions.

Contrarywise, the same mixtures could be used as sources of the 2-isomer in the Tl^{III} oxidation experiments. Here presumably both isomers react, but only the radical cations of the 5,5'-dialkylated 2,2'-bithiophene are persistent enough to be observed.

Oxidation of 2,5-dimethylthiophene (5a) by Tl^{III} in HFP. The results from the previous study⁶ were confirmed, in that irradiation of **5a** under acidic conditions gave an EPR spectrum consisting of a septet of septets centered at $g=2.0067$ ($a^H=0.486$, 0.216 mT; lit. $g=2.0064$ $a^H=0.49$, 0.21 mT). It was suggested⁶ that this spectrum might originate from the radical cation of the 3,3'-dehydrodimer of **5a**, **12**^{•+}, but some doubt was expressed

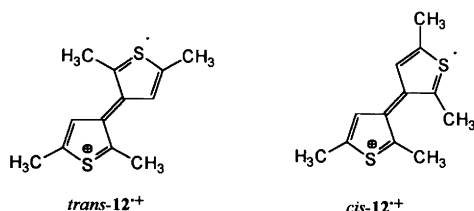
Table 3. Calculated and experimental hfs constants of the radical cations **2a**^{•+}, **2f**^{•+} and **10**^{•+}.

Species	Calculated energy/ kcal mol ⁻¹	Relative energy ^a / kcal mol ⁻¹	a^H /mT		a^H /mT		a^{CH_3} /mT	
			Calcd.	Exp. ^b	Calcd.	Exp.	Calcd.	Exp.
<i>trans</i> - 2a ^{•+}	-7363 40.32	0	H5: -0.841	—	H3: -0.411	—	0.018	—
<i>cis</i> - 2a ^{•+}	-7363 39.87	0.45	H5: -0.880	—	H3: -0.419	—	0.106	—
<i>trans</i> - 2f ^{•+}	-7363 38.49	0	H5: -0.807	0.74	H4: 0.112	0.023	0.526	0.489
<i>cis</i> - 2f ^{•+}	-7363 31.98	6.51	H5: -0.725	—	H4: 0.107	—	0.493	—
<i>trans</i> - 10 ^{•+}	-7370 75.71	0	H3: 0.064	0.033	H5a/b: 1.93	2.04	0.402	0.395
<i>cis</i> - 10 ^{•+}	-7370 75.36	0.35	H3: 0.086	0.023	H5a/b: 1.94	2.02	0.457	0.315
10 ^{•+} , TS ^c	-7370 56.34	19.0	H3: 0.073	—	H5a/b: 1.41	—	0.639	—

^aWithin each pair of isomers. ^bValues in HFP. ^cTransition state between the *cis* and *trans* forms, rings perpendicular.

in view of the missing third coupling to the two 3,3'-hydrogens.

The fact that the 7×7 -line spectrum was accompanied by a second spectrum when **5a** was oxidized by Tl^{III} in HFP–trifluoroacetic acid (7%), now with the second spectrum analyzable in terms of a bithiophene spectrum (Fig. 5) but with a slightly different g value = 2.0037, suggests that we might be dealing with the *trans* and *cis* isomers of $12^{\cdot+}$. Under the conditions given, an equilibrium between the two radical cations is established, meaning that they must be closely similar in redox properties and presumably be structurally very close. The *trans* form can attain a fully planar conformation, in which the delocalization of spin/charge at the sulfur atoms is favoured, thus explaining the higher g value of 2.0067. The missing coupling constant may be due to an undetectably small value, cf. the values 0.033 and 0.021 mT of the isomers of the analogous radical cation $10^{\cdot+}$. In *cis*- $12^{\cdot+}$ coplanarity is not possible, owing to the steric interference of the two methyl groups, and thus the g value is lower, 2.0037.



The CV results for 2,5-dimethylthiophene are in accord with the formation of small amounts of dehydromer upon oxidation (E_{pa} at 0.97 V).

Experimental

Materials. 3-Methyl- (**1a**), 3-ethyl- (**1b**),¹⁹ 3-isopropyl- (**1c**),¹⁹ 3-*tert*-butyl- (**1d**, in admixture with 33% of 2-*tert*-butylthiophene, **3d**),²⁰ 4,4'-Dimethyl-2,2'-bithiophene (**2a**),¹ 2-methyl- (**3a**),²¹ 2-ethylthiophene (**3b**)²¹ and 2,5-dimethylthiophene (**5a**) were either available commercially or from earlier studies. 2-Isopropylthiophene (**3c**)¹ was used as a 63:37 mixture with the 3-isomer. 5,5'-Dimethyl-2,2'-bithiophene (**4a**) was prepared (1974) by T. Frejd²² by reaction of 5-methyl-2-thienyllithium with cupric chloride analogous to the preparation of 2,2'-bithiophene.²³ HFP, trifluoroacetic acid and dichloromethane were of Merck UVASOL[®] quality. (*O*-²H)HFP was from Aldrich (isotopic purity 99%) and (²H₂)SO₄ from Dr. Glaser AG Basel (isotopic purity >99.5%).

Instruments and methods. Cyclic voltammetry was performed by the BAS-100 instrument, in dichloromethane or HFP–Bu₄NPF₆ (0.15 mol dm⁻³) at a Pt button electrode of 2 mm² surface area, using an Ag/AgCl electrode as the reference, and with *iR* compensation. The Pt anode was polished between runs. Potentials given and discussed in the text are given with the Ag/AgCl electrode

as reference. Potentials were calibrated against the internal ferricinium–ferrocene couple (0.43–0.44 V vs. Ag/AgCl in dichloromethane, 0.05 V vs. Ag/AgCl in HFP).

EPR spectra were recorded by the Varian E 109 spectrometer (Barcelona; with the facility for photolysis of the samples in the cavity by light from a 500 W high-pressure Hg lamp) or Upgrade Version ESP 3220-200SH of a Bruker ER-200D spectrometer [Lund; photolyses were performed in the photolysis cavity (ER 4104 OR), using unfiltered light from the 50 W high-pressure Hg lamp from Bruker (ER 202)]. The EPR experiments were performed as described earlier^{1–3} (100 kHz modulation frequency, microwave effect 0.4–1.6 mW, modulation amplitude 0.01–0.04 mT). Simulations were carried out by the public domain program WINSIM²⁴ or by Simfonia[®] (Bruker AG). The *ab initio* and DFT calculations were performed with Gaussian 94²⁵ using a modified treatment²⁶ of the B3LYP hybrid functional. The HF and the DFT calculations were performed at the unrestricted level of theory.

Acknowledgements. Financial support from the Swedish Natural Science Research Council and the Knut and Alice Wallenberg Foundation (to L.E.), and the Spanish Ministry of Education and Science (to L.J.; PB96-0836) is gratefully acknowledged.

References

- Tormo, J., Moreno, F. J., Ruiz, J., Fajari and Juliá, L. *J. Org. Chem.* **62** (1997) 878.
- Alemán, C., Brillas, E., Davies, A. G., Fajari, L. Giró, D., Juliá, L., Pérez, J. J. and Rius, J. *J. Org. Chem.* **58** (1993) 3091.
- (a) Eberson, L., Hartshorn, M. P. and Persson, O. *J. Chem. Soc., Perkin Trans. 2* (1995) 1735; (b) Eberson, L., Hartshorn, M. P., Persson, O. and Radner, F. *Acta Chem. Scand.* **51** (1997) 492; (c) Eberson, L., Hartshorn, M. P., Persson, O., Radner, F. and Rhodes, C. J. *J. Chem. Soc., Perkin Trans. 2* (1996) 1289.
- Kirste, B., Tian, P., Kossmehl, G., Engelmann, G. and Jugelt, W. *Magn. Reson. Chem.* **33** (1995) 70.
- Roncali, J. *Chem. Rev.* **92** (1992) 711; a review on poly(3-alkylthiophenes) can be found in: Andersson, M. R. *Synthesis and Properties of Substituted Poly(thiophenes)*, Thesis, Chalmers University of Technology, Göteborg, Sweden 1995.
- Davies, A. G., Julia, L. and Yazdi, S. N. *J. Chem. Soc., Perkin Trans. 2* (1989) 239.
- Eberson, L., Hartshorn, M. P., Persson, O. and Radner, F. *J. Chem. Soc., Chem. Commun.* (1996) 2105.
- Eberson, L., Hartshorn, M. P., MacCullough, J. J., Persson, O. and Radner, F. *Acta Chem. Scand.* **52** (1998) 1024.
- Rathore, R. and Kochi, J. K. *Acta Chem. Scand.* **52** (1998) 114.
- Belen'kii, L. I. *Chem. Heterocycl. Comp.* (1992) 610.
- Lau, W. and Kochi, J. K. *J. Am. Chem. Soc.* **106** (1984) 6720; 7100.
- Eberson, L., Hartshorn, M. P., Persson, O. Svensson, J. O. *J. Chem. Soc., Perkin Trans. 2* (1995) 1253.
- Taylor, E. C. and McKillop, A. *Acc. Chem. Res.* **3** (1970) 338.

14. (a) Engelmann, G., Kossmehl, G., Heinze, J., Tschuncky, P., Jugelt, W. and Welzel, H.-P. *J. Chem. Soc., Perkin Trans. 2* (1997) 169; (b) Kirste, B., Tian, P., Kossmehl, G., Engelmann, G. and Jugelt, W. *Magn. Reson. Chem.* 33 (1995) 70.
15. Alberti, A., Favaretto, L. and Seconi, G. *J. Chem. Soc., Perkin Trans 2* (1990) 931. See also Ref. 14b.
16. Andersen, M., Ebersson, L. and Hammerich, O. *Unpublished results*.
17. McClelland, R. A. and Steenken, S. *J. Am. Chem. Soc.* 112 (1990) 9648; Mathivanan, N., Cozens, F., McClelland, R. A. and Steenken, S. *J. Am. Chem. Soc.* 114 (1992) 2198.
18. Engels, B., Eriksson, L. A. and Lunell, S. *Adv. Quantum Chem.* 27 (1996) 297; Batra, R., Giese, B., Spichty, M., Gescheidt, G. and Houk, K. N. *J. Phys. Chem.* 100 (1996) 18371; Gauld, E. G., Eriksson, L. A. and Radom, L. *J. Phys. Chem. A* 101 (1997) 1352.
19. Gronowitz, S., Cederlund, B. and Hörnfeldt, A.-B. *Chem. Scr.* 5 (1974) 217.
20. Wynberg, H. and Wiersma, U. E. *J. Org. Chem.* 30 (1965) 1058.
21. King, W. J. and Nord, F. F. *J. Org. Chem.* 14 (1949) 638.
22. Frejd, T. (1974) *Unpublished results*.
23. Gronowitz, S. and Karlsson, H.-O. *Arkiv Kemi* 17 (1960) 89.
24. D. Duling, *Public EPR Software Tools*, National Institute of Environmental Health Sciences, Bethesda, MD 1996.
25. Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C. and Pople, J. A. *Gaussian 94, Revision B.2*, Gaussian, Inc., Pittsburgh, PA 1995.
26. Stephens, P. J., Devlin, J. F., Chabalowski, F. and Frisch, M. J. *J. Phys. Chem.* 98 (1994) 1162.

Received March 9, 1998.