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2,2′-Bithienyl Derivatives: EPR Investigation of Their Radical Ions in Solution, Electrochemical Properties, and Crystal Structure

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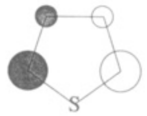
5,5′-Dimethyl-, -diisopropyl-, -di-*tert*-butyl-, and -bis(trimethylsilyl)-2,2′-bithienyl have been prepared (**1**, **2**, **3**, and **4** respectively). The radical cations of **1**, **2**, and **3** have been generated in fluid solution. The electron paramagnetic resonance (EPR) spectra have been analyzed with the help of Hückel/McLachlan and MINDO/3 calculations and show the presence of cis and trans isomers, although X-ray diffraction studies of **1** and **4** have identified only the trans isomer in solid state. MINDO/3 predicts the observation of both isomers of $\mathbf{1}^{\bullet+}$ on the EPR timescale by estimating the barrier to ring rotation. This value is much higher than in the parent molecule, which fits in with the observation of presumably only one isomer by nuclear magnetic resonance (NMR). If the 2- and 5-positions are not blocked, oligomerization occurs: 2-methylthiophene gives the 5,5′-dimethyl-2,2′-bithienyl radical cation ($\mathbf{1}^{\bullet+}$), and 2,2′-bithienyl itself gives the poly-2,2′-bithienyl radical cation. The radical anion of **4** (and of its 3,3′-dideuterated derivative) has been generated, but the lines in the EPR spectrum are broad, and only one isomer can be detected. Oxidation potentials corresponding to the anodic peak potentials of the irreversible oxidation peaks for **1**, **2**, and **3** are lower than that of 2,2′-bithienyl as expected, while that of **4** is only slightly higher, which is consistent with the weak electron-withdrawing effect of the trimethylsilyl substituent. On the other hand, a quasireversible redox couple ($E^0 = -2.34$ V vs SCE) has been found for the reduction of **4**.

Introduction

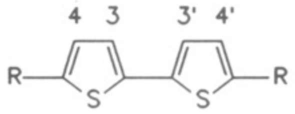
Increasing interest has been devoted to polythiophene as an organic conducting polymer.[2] Polythiophene and its derivatives appear to be good candidates because of their high chemical and electrochemical stability in both oxidized and neutral states. It is well known that conjugated polymers and particularly polythiophene develop charged defects in the oxidized state, polarons (radical cations) and bipolarons (dications), which are responsible for the conducting properties of these condensed systems.[3]

The analysis of the spin density distribution in the small and repeated units of polythiophene constitutes a good approach for describing the distribution of polarons over the chain.

Our relation with this topic arose in connection with the detection and study by electron paramagnetic resonance (EPR) in fluid solution of the oxidized states, radical cations, of some thiophene derivatives obtained by means of chemical reagents.[4] From the values of the hyperfine coupling constants, which were in accord with the values obtained from experiments on Freon matrices and from INDO calculations, it was concluded that the SOMO of thiophene has the form



We have now been concerned with the 2,2′-bithienyl system, and in particular with the following disubstituted derivatives: 5,5′-dimethyl- (**1**), 5,5′-diisopropyl- (**2**), 5,5′-di-*tert*-butyl- (**3**), and 5,5′-bis(trimethylsilyl)-2,2′-bithienyl (**4**).



(1): R= CH_3
(2): R= $CH(CH_3)_2$
(3): R= $C(CH_3)_3$
(4): R= $Si(CH_3)_3$

Herein, we will describe the EPR results on radical ions of **1**, **2**, **3**, and **4** generated in situ, the determination of their redox potentials by cyclic voltammetry, and the X-ray structure determination of **1** and **4**.

Synthesis and Structural Identification

5,5′-Dimethyl-2,2′-bithienyl (**1**), a well-known bithienyl derivative, was synthesized by a new procedure starting

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[2] Tourillon, G. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, chapter 9.

[3] Frommer, J. E.; Chance, R. R. In *Electrical and Electronic Properties of Polymers: A State-of-the-Art Compedium*; Kroschwitz, J. I., Ed.; John Wiley: New York, 1988; p 56.

[4] Davies, A. G.; Juliá, L.; Yazdi, S. N. *J. Chem. Soc., Chem. Commun.* **1987**, 929. Davies, A. G.; Juliá, L.; Yazdi, S. N. *J. Chem. Soc., Perkin Trans. 2* **1989**, 239.

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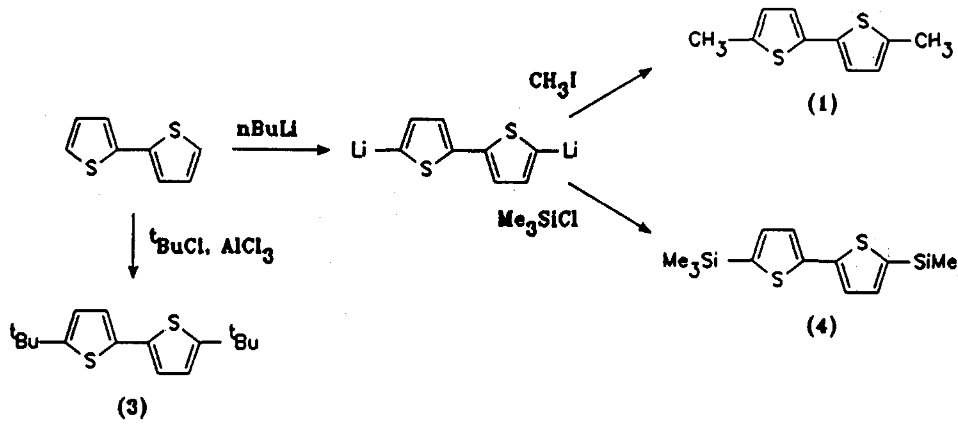
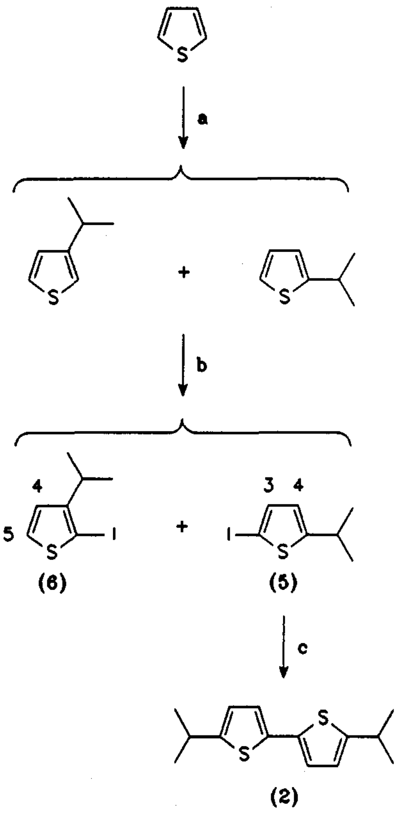
Scheme I



Scheme II[a]



[a] Reagents: (a) isopropyl chloride, AlCl$_3$, and CH$_2$Cl$_2$; (b) H$_5$IO$_6$, I$_2$, and AcOH–H$_2$O–H$_2$SO$_4$; (c) Zn, NiCl$_2$(PPh$_3$)$_2$, NBu$_4$I, and THF.

from 2,2′-bithienyl, which consisted of lithiation with *n*-BuLi in a mixture of hexane–THF and then condensation by slow addition of methyl iodide.

The dilithio derivative was also used in the syntheses of 5,5′-bis(trimethylsilyl)-2,2′-bithienyl (**4**) by a coupling reaction with trimethylsilyl chloride as reported in the literature.[5]

5,5′-Di-*tert*-butyl-2,2′-bithienyl (**3**) was prepared by a Friedel–Crafts reaction on 2,2′-bithienyl catalyzed by AlCl$_3$ and using an excess of *tert*-butyl chloride as the alkylating agent (Scheme I).

The synthesis of 5,5′-diisopropyl-2,2′-bithienyl (**2**) was performed by the procedure outlined in Scheme II. Alkylation of thiophene with isopropyl chloride in the presence of AlCl$_3$ gave a mixture of 2- and 3-isopropylthiophenes[6] with a predominance of the first isomer. This mixture was then iodinated using a reported method,[7] in a similar manner to the iodination of 2- and 3-methylthiophenes which gives 2-iodo-5-methyl- and 2-iodo-3-methylthiophenes, respectively.[8] The mixture of iodoisopropylthiophenes **5** and **6** was clearly identified by ^{1}H NMR. In Figure 1 the signals due to the ring protons are shown.

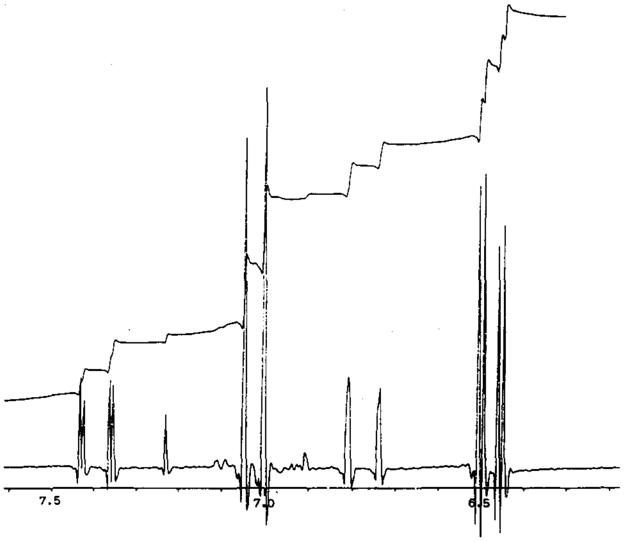


Figure 1. ^{1}H NMR spectrum (80 MHz) of the isomeric mixture of **5** and **6** (CDCl$_3$).

The broad doublet centered at $\delta = 6.77$ ($J_{4,5} = 4.64$ Hz) and the doublet of doublets at $\delta = 7.40$ ($J_{4,5} = 4.64$ Hz, $J' = 0.8$ Hz) were assigned to H-4 and H-5 of **6**, respectively, by analogy with the spectrum of 2-iodo-3-methylthiophene;[9] hence, the doublet at $\delta = 7.03$ ($J_{3,4} = 3.52$ Hz) and the doublet of doublets at $\delta = 6.47$ ($J_{3,4} = 3.52$ Hz, $J' = 0.9$ Hz) were assigned to H-3 and H-4 of **5**, respectively, by analogy with the spectrum of 2-iodo-5-methylthiophene.[9] Reductive dimerization of this mixture of iodoisopropylthiophenes **5** and **6** gave a complex mixture from which a small amount of 5,5′-diisopropyl-2,2′-bithienyl (**2**) was separated by recrystallization.

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[5] Lemaire, M.; Büchner, W.; Garreau, R.; Hoa, H. A.; Guy, A.; Roncali, J. *J. Electroanal. Chem.* **1990**, *281*, 293.

[6] Belen'kii, L. I.; Yakubov, A. P. *Tetrahedron* **1984**, *40*, 2471.

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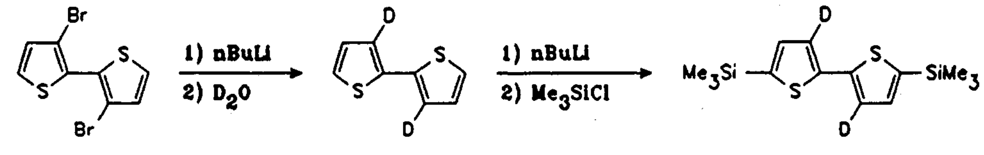
[8] Krische, B.; Hellberg, J.; Lilja, C. *J. Chem. Soc., Chem. Commun.* **1987**, 1476.

[9] Takahashi, K.; Ito, I.; Matsuki, Y. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 605.

Scheme III



(7) (8)

Table I. Selected ^1H NMR Data for 2,2'-Bithienyls

	chemical shifts,[a] δ, ppm	
compd	3,3'	4,4'
1[b]	6.87	6.62
2	6.87	6.69
3	6.90	6.67
4	7.22	7.11
8	-	7.12

[a] In $CDCl_3$, in 80 MHz. [b] Although ^1H NMR data are reported in the literature,[8] coupling between H-4 and H-4' with the α-H of the substituent in 5 and 5', respectively, was not mentioned.

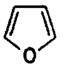
The synthesis of 5,5'-bis(trimethylsilyl)-2,2'-bithienyl-3,3'-d_2 (8) was carried out as follows: lithiation of 3,3'-dibromo-2,2'-bithienyl with *n*-BuLi at low temperature and quenching the reaction mixture with an excess of D_2O gave 2,2'-bithienyl-3,3'-d_2 (7). Then, 8 was obtained from 7 by a similar process as that used in preparing 4 (Scheme III).

Selected ^1H NMR data for 1–4 and 8 are listed in Table I. The chemical shifts of the two ring pairs of protons are distinguished by the small coupling of H-4 and H-4' with the α-H of the substituent in the 5 and 5' positions[5] for bithienyls 1 and 2 (see Experimental Section). The downfield shift of both ring pairs in 4, due to the deshielding effect of trimethylsilyl compared with alkyl substituents, is also significant. The absolute assignment of the chemical shifts in 4 is determined by dideuteration in the 3,3'-positions (8).

Electron Paramagnetic Resonance Results

Electron paramagnetic resonance (EPR) spectroscopy provides a powerful method of studying the properties of semioccupied molecular orbitals. Thus, information on the highest occupied molecular orbital (HOMO) of a molecule is obtained through formation of its radical cation. Analysis of the hyperfine coupling constants between the unpaired electron and magnetically active nuclei in the molecule provides data concerning the electron distribution in the HOMO.

We have been able to generate the radical cations from a variety of furans (9), thiophenes (10), and pyrroles (11) by photolyzing the substrates in the presence of trifluoroacetic acid, sulfuric acid, or trifluoroacetic acid containing mercury(II) or thallium(III) trifluoroacetate.[4,10] Only when 2- and 5-positions of those heterocycles are blocked with alkyl groups, are the radical cations stable enough to be detected and studied by EPR spectroscopy.



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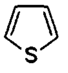

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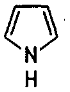
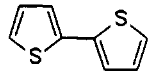


(11)

When thiophene itself was photolyzed in trifluoroacetic acid containing thallium(III) trifluoroacetate, the solution showed a strong singlet spectrum, *g* 2.0034, ΔH_{pp} 1.45 G.[11] Only in frozen freon solutions, have Shiotani et al.[12] and Symons et al.[13] detected the monomeric radical cation.

We have now focused our attention on 2,2'-bithienyls. As far as we know there are no report concerning the generation of bithienyl radical cations, with the exception of a recent study by Alberti;[14] the observation of a weak EPR spectrum by oxidation of the 2,2'-bithienyl itself (12)



(12)

in CH_2Cl_2/CF_3COOH (1:1), which is attributed to its radical cation, was reported, although assignment was not unambiguous.

We have carried out the oxidation of 2,2'-bithienyl itself in trifluoroacetic acid containing thallium(III) trifluoroacetate and, similarly as it occurs with thiophene, it quickly reacted and a very dark solid separated from solution.[15] This solid, washed and dried, showed in the EPR a singlet, *g* 2.0027, ΔH_{pp} 1.62 G. A more detailed analysis of this paramagnetic solid by infrared spectroscopy showed that a 5,5'-polymerization of 2,2'-bithienyl took place to give a doped polymer, which rendered a neutral poly[5,5'-(2,2'-bithienyl)] of very good quality after a compensation process. This is consistent with the observation by Alberti that the oxidation of 2,2-bithienyl in the presence of an excess of trifluoroacetic acid[14] gave rise to an EPR spectrum which coincided with that of 2,2',5',2'',5'',2'''-quarterthienyl, suggesting that the radical cation of 2,2'-bithienyl, which is formed, is very unstable and dimerizes.

However, we have been able to detect 2,2'-bithienyl radical cations and to interpret their spectra in terms of the simple monomeric species when alkyl groups are present in the 5- and 5'-positions which are the more active polymerization sites.

Thus, photolysis of 5,5'-dimethyl- (1), 5,5'-diisopropyl- (2), and 5,5'-di-*tert*-butyl-2,2'-bithienyl (3) in trifluoroacetic acid with or without mercury(II) or thallium(III) trifluoroacetate gave rise to strong and well-resolved spectra. The same spectra are shown when a CH_2Cl_2 solution of each 2,2'-bithienyl containing $AlCl_3$ is photolysed at low temperature. All three radical cations are stable even at room temperature. Under both conditions,

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(10) Avila, D. N.; Davies, A. G. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3243. Davies, A. G.; Schiesser, C. H. *J. Organometal. Chem.* **1990**, *389*, 301. Avila, D. N.; Davies, A. G. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1111.

(11) Juliá, L.; Davies, A. G.; Rueda, D. R.; Calleja, F. J. B. *Chem. Ind.* **1989**, 78.

(12) Shiotani, M.; Nagata, Y.; Tasaki, M.; Sohma, J.; Shida, T. *J. Phys. Chem.* **1983**, *87*, 1170.

(13) Rao, D. N. T.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1983**, 135.

(14) Alberti, A.; Favaretto, L.; Seconi, G.; Pedulli, G. F. *J. Chem. Soc., Perkin Trans. 2* **1990**, 931.

(15) Giménez, E.; Juliá, L. Unpublished results.

Table II. Experimental Hyperfine Coupling Constants (G) for Radical Cations from 1, 2, and 3

bithienyl	isomeric distribution, %	$a_{3,3'}$	$a_{4,4}$	$a_{5,5'}$	g	ΔH_{pp} (G)
1[a]	67	3.91	0.94	9.08 (6 H)	2.00285	0.06
	33	4.12	0.70	9.24 (6 H)	2.00281	0.06
2[b]	60	3.82	0.75	7.52 (2 H), 0.25 (12 H)	2.00275	0.08
	40	3.77	0.78	7.68 (2 H), 0.26 (12 H)	2.00266	0.08
3[c]	56	4.13	1.05	0.35 (18 H)	2.00265	0.09
	44	4.03	1.08	0.36 (18 H)	2.0062	0.09

[a] In CH_2Cl_2–$AlCl_3$ at −80 °C. [b] In CF_3COOH–$Hg(CF_3COO)_2$ at −10 °C. [c] In CH_2Cl_2–$AlCl_3$ at 10 °C.

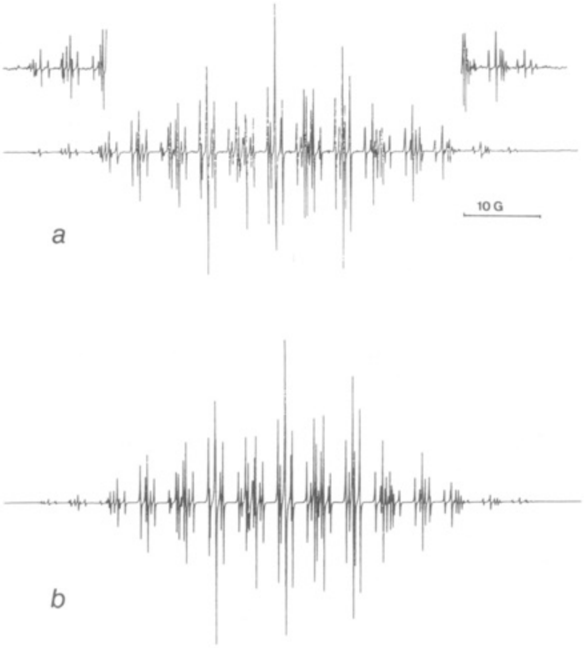
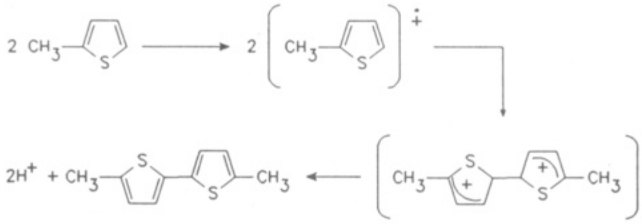


Figure 2. (a) ESR spectrum of the 5,5′-dimethyl-2,2′-bithienyl radical cation $1^{\cdot+}$ in CH_2Cl_2–$AlCl_3$ at 193 K. (b) Computer simulation using the data in Table II.

these spectra result from the superimposition of two radical species, in a ratio of about 3:2, which we believe correspond to the trans and cis conformations. These isomers show very similar g factors and slightly different hyperfine splitting (hfs) constants (see Table II). The EPR spectra obtained from **1**, **2**, and **3**, and their computer simulations are displayed in Figures 2, 3, and 4, respectively.

Photolysis of 2-methylthiophene under the same conditions displayed the same spectrum as did **1**, which established that oxidative dimerization to bithienyl mainly occurs through the most reactive 5 position and that the cation radical of thienyls with one of the α-positions free are not stable enough to be detected by EPR.



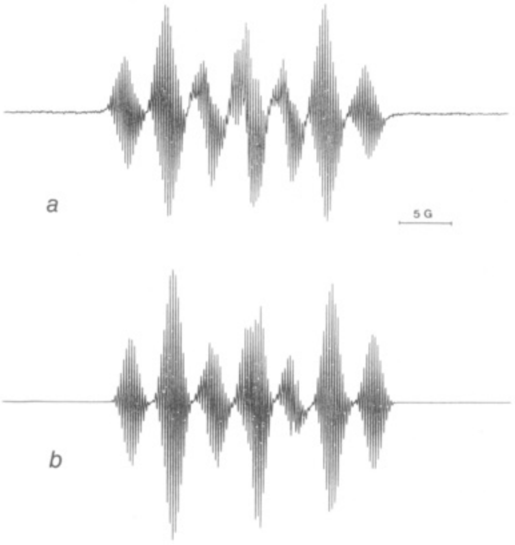


Figure 3. (a) ESR spectrum of the 5,5′-diisopropyl-2,2′-bithienyl radical cation $2^{\cdot+}$ in CF_3COOH–$Hg(CF_3COO)_2$ at 263 K. (b) Computer simulation using the data in Table II.

In each case, the spectra of both isomers can be analyzed in terms of hyperfine coupling by two pairs of protons at the 3,3′ and 4,4′ positions and by the α-protons of the substituents at the 5,5′ positions (see Table II). The assignment of the coupling constants to the various positions was made by comparison with the EPR spectrum of the biphenyl radical cation and from the results of theoretical calculations. The low g values are evidence of the small electron density at the sulfur center in the HOMO.

On the other hand, EPR spectroscopy also provides information on the lowest unoccupied molecular orbital (LUMO) of a molecule through formation of its radical anion. Thus, treatment of 5,5′-bis(trimethylsilyl)-2,2′-bithienyl (**4**) in degassed tetrahydrofuran with potassium leads to the detection of a radical specie which was attributed to the radical anion (Figure 5). The hyperfine splittings reported in Table III have been assigned by comparison with the spectrum of 3,3′-dideutero-5,5′-bis(trimethylsilyl)-2,2′-bithienyl (8) (Figure 6). The high g values indicate a relatively high electron density at the sulfur centers.

In addition, ^{29}Si satellites (I = $^1/_2$, 4.7% natural abundance) are noticeable in $\mathbf{4}^{\cdot-}$ as well-separated lines. The value of the ^{29}Si hyperfine coupling constant (Table III) is very close to that in the spectrum of the 4,4′-bis(trimethylsilyl)biphenyl radical anion (2.24 G).[16]

In contrast to the bithienyl radical anion, where the EPR spectrum indicates the presence of the cis and trans rotamers,[17] it is not possible to detect both isomers in the trimethylsilyl derivatives $\mathbf{4}^{\cdot-}$ and $8^{\cdot-}$ probably because of the large line widths.

The computer simulation of the spectrum of $8^{\cdot-}$ (Figure 6) takes into account the spectra corresponding to the monodeuterated and nondeuterated bithienyl radical anions, which are present as impurities of the main dideuterated radical anion. To simulate both contributions, the same value of a H-3 as in $8^{\cdot-}$ has been used.

Theoretical estimation of the proton hyperfine coupling constants for the radical ions of **1** and **4** has been carried out using three different quantum mechanical methods,

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(16) Curtis, M. D.; Allred, A. L. *J. Am. Chem. Soc.* **1965**, *87*, 2554.

(17) Cavalieri d'Oro, P.; Mangini, A.; Pedulli, G. F.; Spagnolo, P.; Tiecco, M. *Tetrahedron Lett.* **1969**, 4179.

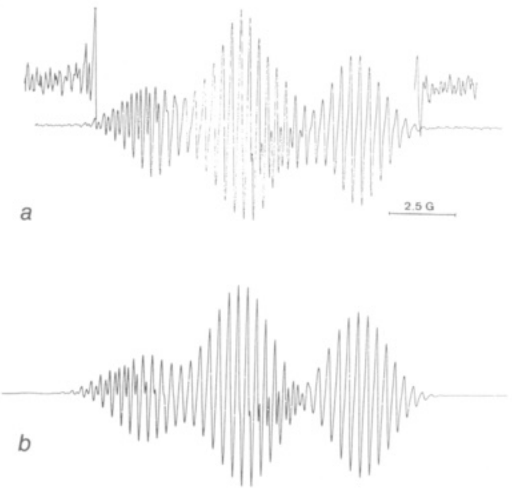


Figure 4. (a) ESR spectrum of the 5,5′-di-*tert*-butyl-2,2′-bithienyl radical cation $3^{\bullet+}$ in CH_2Cl_2–$AlCl_3$ at 283 K. (b) Computer simulation using the data in Table II.

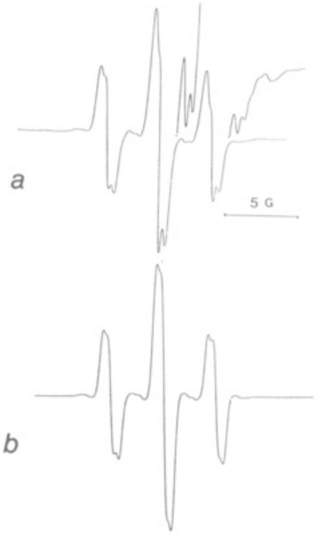


Figure 5. (a) ESR spectrum of the 5,5′-bis(trimethylsilyl)-2,2′-bithienyl radical anion $4^{\bullet-}$ in THF–K at 203 K. (b) Computer simulation using the data in Table III.

Table III. Experimental Hyperfine Coupling Constants (G) for Radical Anions from 4 and 8

bithienyl	$a_{3,3'}$[a]	$a_{4,4'}$	a_{Si}	g	ΔH_{pp} (G)
4	3.53	0.40	2.98	2.00465	0.26
8	0.52	0.40		2.00458	0.26

[a] The $a(4)/a(8)$ is ca. 6.514, as required for the magnetogyric ratio relation (γ_H/γ_D).

namely on the one hand, the method proposed by McLachlan,[18] and on the other, the semiempirical Hartree–Fock methods INDO[19] and MINDO/3.[20]

McLachlan's method was proposed in the late fifties and is an extension of the Hückel Molecular Orbital method in which an unrestricted wavefunction is used. Despite its simplicity, the method provides good estimates of the hfs constants and consequently has been widely used.

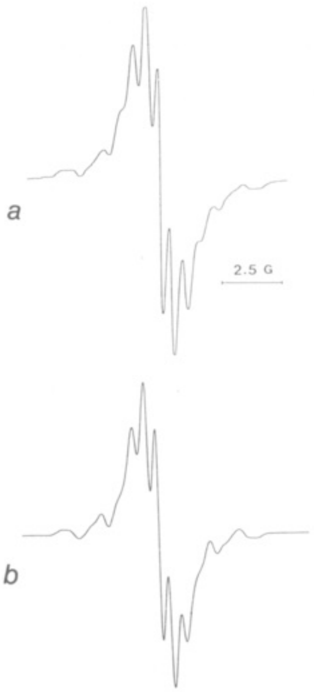
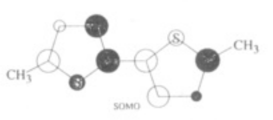


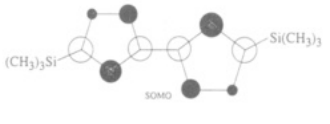
Figure 6. (a) ESR spectrum of 5,5′-bis(trimethylsilyl)-2,2′-bithienyl-3,3′-d_2 radical anion $8^{\bullet-}$ in THF–K at 203 K. (b) Computer simulation using the data in Table III.

Nevertheless, its reliability depends on the selection of the appropriate heteroatom parameters. The parameters used in the present calculations were modified from those published in the literature[21,22] in order to provide good hfs constants for thiophene radical ions and their substituted derivatives. The heteroatom parameters h_M corresponding to the Coulomb integral, $\alpha_M = \alpha + h_M\beta$ and k_{CM} of the resonance integral $\beta_{CM} = k_{CM}\beta$ are 1.0 and 0.86 for S, −0.3 and 1.0 for Me, and −1.4 and 0.2 for Me_3Si, respectively.

Thus, according to McLachlan's method, the SOMO of the radical cation of 1 and the radical anion of 4 have the following form:



$1^{\bullet+}$



$4^{\bullet-}$

The INDO method has proven to be a reliable method for estimating hfs constants and has been traditionally used in the literature.[23] Again computed spin densities from MINDO/3 wave functions without spin annhilation give reliable estimates of the EPR coupling constants for a wide range of compounds[24] and show a superior performance over the AM1 and MNDO methods.[25] However, it gives poor results for silyl derivatives and therefore only MINDO/3 calculations were performed on compound 1. Calculations were carried out on the MINDO/3-optimized geometries, available as supplementary material, which have been shown to provide the best estimates.[25,26]

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Table IV. McLachlan, INDO, and MINDO/3 Calculated Hyperfine Coupling Constants for Radical Cation $1^{\bullet+}$ and Radical Anion $4^{\bullet-}$

	method	$a_{3,3'}$	$a_{4,4'}$	$a_{5,5'}$
$1^{\bullet+}$	McLachlan	3.6	1.2	
	INDO	6.5	7.5	7.6
	MINDO/3	3.3	4.8	8.8
$4^{\bullet-}$	McLachlan	3.0	1.3	
	INDO	8.4	7.4	

Using the McConnell approximation,[27] hfs constants were computed from its linear relationship with the electron spin densities. A proportionality constant of −539.86 G was used for the INDO method[19] and −397 G for MINDO/3.[25]

The hfs constants computed with the different methods are listed in Table IV. Comparison between experimental and observed hfs constants is good for both McLachlan and MINDO/3 theoretical results. Surprisingly, INDO-computed hfs constants display very poor agreement with experimental values. This may be attributed to some deficiences in the second row element's parametrization.

By MINDO/3 calculations and assuming a planar geometry of the molecules, we have been able to estimate the barrier to ring rotation in 5,5′-dimethyl-2,2′-bithienyl in terms of the energies of the cis, trans, and orthogonal isomers in the neutral molecule and in the radical cation. The trans conformation is as stable as the cis in the neutral molecule and more stable by 0.8 kcal mol^{-1} in the radical cation. Moreover, the orthogonal isomer is much more unstable in the radical cation (9.8 kcal mol^{-1}) than in the neutral molecule (0.9 kcal mol^{-1}) by reference to the trans isomer. These results indicate that while the intramolecular rotation is practically free in the parent compound 1, which fits in with the observation of presumably only one isomer by NMR, it is much more difficult in the radical cation $1^{\bullet+}$, which is expected to be held predominantly in both planar conformations, cis and trans, on the EPR timescale to be observed. This is in accord with an analysis of the HOMO orbital of 1 which presents an out-of-phase combination between the carbons linking both rings. Thus, formation of the radical cation reduces the π-antibonding interaction between these carbons and causes the origin of the relative rigidity against the free rotation.

Redox Properties

The electrochemical technique of cyclic voltammetry has been used to study the redox properties of alkylthiophenes and thiophene oligomers which are of interest for designing polymeric conductors.

Cyclic voltammograms for the oxidation of compounds 1–4 as well for 2-2′-bithienyl (12) for comparison in DMF with 0.1 M TBAP as supporting electrolyte displayed a diffusion-controlled irreversible anodic peak (peak O) at all scan rates tested. This peak can be observed in Figure 7 where typical cyclic voltammograms associated to the oxidation of 2,2′-bithienyl and its bis(trimethylsilyl) derivative at v = 0.050 V s^{-1} are presented. For peak O of each compound, the difference between the anodic peak and half-peak potentials ($E^a_p - E^a_{p/2}$) is always found to be between 80–90 mV, whereas E^a_p varies linearly with log v, with a slope close to 55–58 mV/decade. These parameters agree with the theoretical values expected for an irreversible one-electron reaction with a transfer coefficient (α) close to 0.5 [theoretical values for an irreversible E mechanism at 25.0 °C:[28] ($E^a_p - E^a_{p/2}$) = 48/α; slope of E^a_p vs log v linear plot = 29.6/α]. These findings establish that the oxidation of compounds 1–4 and 12 at peak O is initiated by an irreversible one-electron step (which is rate-determining) leading to the formation of its radical cation, according to the general process:

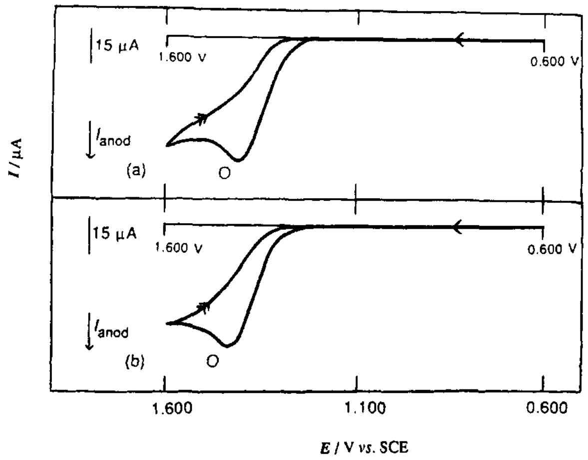

Figure 7. Cyclic voltammograms for the oxidation of (a) 1.0 mM 2,2′-bithienyl (12) and (b) 1.0 mM 5,5′-bis(trimethylsilyl)-2,2′-bithienyl (4) in DMF containing 0.1 M TBAP, at a Pt electrode, at a scan rate of 0.050 V s^{-1} and at 25.0 °C. Starting potential 0.600 V and reversal potential 1.600 V.

$$A \rightarrow A^{\bullet+} + e^-$$

where A denotes any compound 1–4 and 12 and $A^{\bullet+}$ the corresponding radical cation. The irreversibility of peak O can then be explained on the basis that the initially electrogenerated radical cations are too unstable in DMF and decompose rapidly, although for compounds 1–4 the most active positions to undergo oxidative polymerization (their terminal α-positions) are blocked with alkyl or trimethylsilyl substituents. For the dimethyl derivative 1 however, a small second anodic peak, appearing at ca. 250 mV more positive potential than its peak O, was also observed at low scan rates (≤0.050 V s^{-1}), which can be ascribed to the one-electron oxidation of its radical cation to form the dication. No peak associated with dication formation could be detected for 2,2′-bithienyl 12 and compounds 2–4 within the accessible potential range.

Taking into account that compounds 1–4 and 12 undergo the same kinetic behavior in peak O due to the initial formation of their radical cations by an irreversible E mechanism, their anodic peak potentials at a given scan rate can be used as comparative oxidation potentials. Table V summarizes the anodic peak potentials found for peak O of these compounds at v = 0.050 V s^{-1}. As can be seen, the oxidation potentials of all the dialkylated 2,2′-bithienyls (compounds 1–3) are lower than that of 2,2′-bithienyl due to the $+I$ effect of the alkyl groups, the dimethyl derivative 1 having the lowest value because of the additional hyperconjugation corresponding to the σ-(C–H)–π interaction. In addition, it should be remarked that the bis(trimethylsilyl) derivative 4 is more difficult to oxidize than 1, 2, and 3, and its oxidation potential is only slightly higher than that of 12 (see also Figure 7), which is consistent with the weak electron-withdrawing effect of the trimethylsilyl substituent.

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Table V. Oxidation Potentials of 2,2′-Bithienyls in DMF Containing 0.1 M TBAP and at 25.0 °C[a]

compound	E_a^p/V^b
2,2′-bithienyl (**12**)	1.41[d]
5,5′-Dimethyl-2,2′-bithienyl (**1**)	1.21, 1.45[c]
5,5′-Diisopropyl-2,2′-bithienyl (**2**)	1.26
5,5′-Di-*tert*-butyl-2,2′-bithienyl (**3**)	1.27
5,5′-Bis(trimethylsilyl)-2,2′-bithienyl (**4**)	1.44[d]

[a] Oxidation potentials correspond to the anodic peak potentials of the irreversible oxidation peaks found in cyclic voltammograms performed at a Pt electrode and at a scan rate of 0.050 V s^{-1}. [b] Anodic peak potentials vs SCE (NaCl-saturated solution). [c] Anodic peak potential for the second oxidation peak. [d] Reported $E^a{}_p$ values for **12** and **4** are 1.32 and 1.14 V in CH_3CN, respectively.[5]

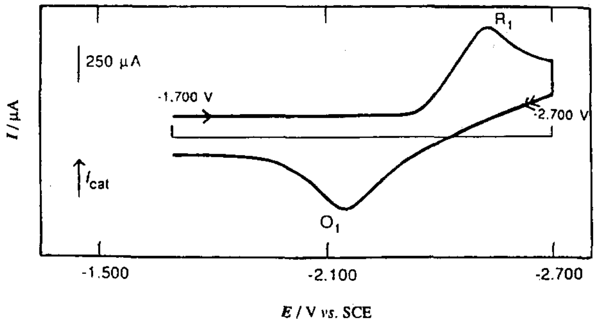

Figure 8. Cyclic voltammogram for the reduction of 1.0 mM 5,5′-bis(trimethylsilyl)-2,2′-bithienyl (**4**) in DMF containing 0.1 M TBAP, at a Pt electrode, at a scan rate of 100 V s^{-1} and at 25.0 °C. Starting potential −1.700 V and reversal potential −2.700 V.

On the other hand, compounds **1**–**3** and **12** did not exhibit any defined reduction peak in cyclic voltammetry. The bis(trimethylsilyl) derivative **4**, which is expected to be the most easily reducible compound, displayed a multireduction process at low scan rates, partially overlapped with the reduction of the medium, and a well-defined quasireversible redox couple, O_1/R_1, from $v = 10$ V s^{-1}, with a standard potential (E^0) of −2.34 V vs SCE. Figure 8 shows a cyclic voltammogram recorded for this compound at 100 V s^{-1}, where this redox couple can be observed. The O_1/R_1 couple can be ascribed to the equilibrium between **4** and radical anion $\mathbf{4}^{\bullet-}$.

$$\mathbf{4} + e^- \rightleftharpoons \mathbf{4}^{\bullet-}$$

At scan rates lower than 10 V s^{-1}, this radical anion decomposes completely and for this reason, peak O_1 is not observed under these experimental conditions. The low stability of this radical anion accounts for the fact that the formation of more unstable radical anions in the reduction of compounds **1**–**3** and **12** cannot be detected by cyclic voltammetry.

Molecular Structure of 1 and 4

It has been difficult to obtain good single crystals of polythienyls for X-ray diffraction studies; only a few reports have been published so far and all them have shown that in the crystal the two thienyl rings are trans coplanar.[29] In addition, large experimental errors in bond lengths and angles have been found in 2,2′-bithienyl **12** because of decomposition of crystals during X-ray exposures.[30] We have now succeeded in obtaining good crystals of 5,5′-dimethyl-2,2′-bithienyl (**1**) and 5,5′-bis(trimethylsilyl)-2,2′-bithienyl (**4**) and their X-ray molecular structure are shown in Figure 9 and 10, respectively.[31] In both cases, the bithienyl skeleton is planar with a transoid arrangement and has a center of symmetry at the midpoint of the C1–C1′ bond (C2–C2′ according to the IUPAC nomenclature). The bond distances and angles for **1** and **4** are reported in Tables VI and VII, respectively. All the C–S bond distances for both structures are in good agreement with

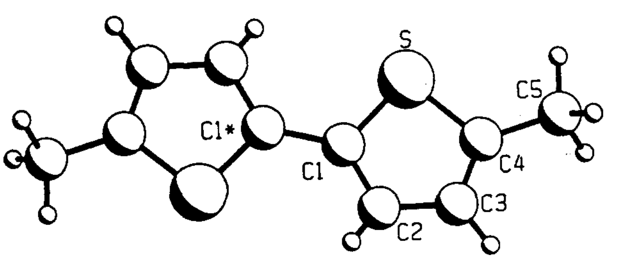

Figure 9. The molecular structure of 5,5′-dimethyl-2,2′-bithienyl (**1**) with the X-ray atom-numbering scheme.

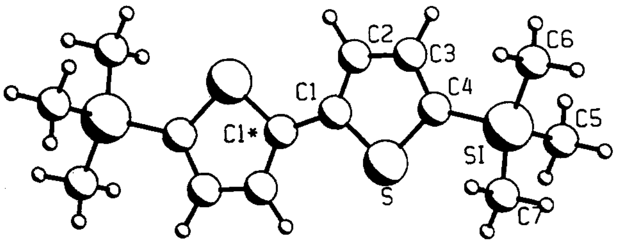

Figure 10. The molecular structure of 5,5′-bis(trimethylsilyl)-2,2′-bithienyl (**4**) with the atom-numbering scheme.

Table VI. Interatomic Distances (Å) and Angles (deg) with ESDs in Parentheses for Non-H-Atoms for 5,5′-Dimethyl-2,2′-bithienyl (1)

C1–S	1.719(2)	C4–S–C1	92.9(1)
C4–S	1.721(3)	C2–C1–S	109.8(2)
C2–C1	1.370(3)	C3–C2–C1	113.2(2)
C1–C1′	1.454(4)	C4–C3–C2	113.8(2)
C3–C2	1.408(3)	C3–C4–S	110.3(2)
C4–C3	1.349(3)	C5–C4–S	120.5(2)
C5–C4	1.502(3)	C5–C4–C3	129.3(2)

Table VII. Interatomic Distances (Å) and Angles (deg) with ESDs in Parentheses for Non-H-Atoms for 5,5′-Bis(trimethylsilyl)-2,2′-bithienyl (4)

C4–Si	1.861(2)	C5–Si–C4	108.9(1)
C5–Si	1.865(3)	C6–Si–C4	107.7(1)
C6–Si	1.850(3)	C6–Si–C5	111.0(1)
C7–Si	1.864(3)	C7–Si–C4	109.2(1)
C1–S	1.723(2)	C7–Si–C5	108.5(1)
C4–S	1.726(2)	C7–Si–C6	111.5(2)
C2–C1	1.368(3)	C4–S–C1	94.2(1)
C1–C1′	1.446(3)	C2–C1–S	109.5(1)
C3–C2	1.412(3)	C3–C2–C1	113.3(2)
C4–C3	1.374(2)	C4–C3–C2	114.7(2)
		S–C4–Si	123.1(1)
		C3–C4–Si	128.5(1)
		C3–C4–S	108.4(1)

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those reported for other bithienyls. The presence of 5,5′-dimethyl- and 5,5′-bis(trimethylsilyl) substituents makes some differences in bond lengths and angles in comparison with 2,2′-bithienyl itself, resulting in minor deviations from $2mm$ (C_{2v}) symmetry of the bithienyl rings. The enlargement of the S–C$_4$–Si bond angle (S–C$_5$–Si according to the IUPAC nomenclature) is due most probably to the relief of steric interference between the S atom and the $(CH_3)_3$-Si substituent group, which results also a reduction of the C$_3$–C$_4$–S bond angle (C$_4$–C$_5$–S according to the IUPAC nomenclature).

Experimental Section

General Procedures. Melting points were obtained by using a Köfler microscope "Reichert" and are uncorrected. The UV and ^{1}H NMR spectra were recorded with Beckman Acta M-VI and Bruker WP805Y spectrometers, respectively. All ^{1}H NMR spectra were obtained using $CDCl_3$ solvent and tetramethylsilane as internal reference. EI mass spectra were obtained on a TS-250 (VG, Manchester, UK) and accurate mass determinations were obtained on a EI Autospec (VG, Manchester, UK). GC-MS (EI) spectra were determined on a Hewlett-Packard Model 5995 C using an HP5 (methyl phenyl silicone, 5%) capillary column (30 m × 0.25 mm i.d.). Solvents were dried and purified before use. THF was freshly distilled from sodium benzophenone ketyl, and 3,3′-dibromo-2,2′-bithienyl was prepared according to a published procedure.[32]

EPR Experiments. EPR spectra were recorded using a Varian E 109 spectrometer with the facility for photolysis of samples in the cavity with light from a 500-W high-pressure mercury arc. 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. To prepare the radical cations, solutions of the substrates in CH_2Cl_2–$AlCl_3$ or Hg(II)–CF_3COOH or Tl(III)–CF_3COOH were degassed at low temperatures (0 °C) by passing a stream of dry nitrogen through the solution to remove oxygen and then inserted into the cavity at low temperatures (193 K with CH_2Cl_2 and 263 K with CF_3COOH). To prepare the radical anions the degassed solutions of the substrates in THF in a sealed silica tube were brought into contact with a sublimed potassium mirror and then inserted into the cavity at low temperature (203 K).

Cyclic Voltammetry. The cyclic voltammetric experiments were conducted in a three-electrode cell under an argon atmosphere. A platinum sphere with an area of 0.093 cm^2 was used as the working electrode and a Pt wire as the counter electrode. The reference electrode was a SCE (NaCl-saturated solution) that was connected to the cell by a salt bridge containing a 0.1 M TBAP–DMF solution. The temperature of test solutions and of SCE was maintained at 25.0 ± 0.1 °C. Cyclic voltammetric measurements were carried out with a PAR 175 universal programmer connected to an Amel 551 potentiostat. Cyclic voltammograms performed at a scan rate (v) lower than 0.2 V s^{-1} were recorded directly on a Philips 8043 X-Y recorder, whereas those obtained at higher scan rates were previously recorded on a Nicolet 3091 digital storage oscilloscope. The ohmic drop compensation of all voltammetric measurements was achieved with a positive feedback network using the same instruments. Solutions of 1.0 mM substrate concentration in DMF with 0.1 M TBAP as supporting electrolyte were studied. The volume of all test solutions was 25 cm^3. Cyclic voltammograms corresponding to the oxidation of each substrate were recorded in the scan rate range 0.02–0.2 V s^{-1}, whereas those associated to its reduction in the v interval 0.02–100 V s^{-1}.

5,5′-Dimethyl-2,2′-bithienyl (1). *n*-BuLi in hexane (1.4 M, 11.3 mL, 15.82 mmol) was added dropwise to a solution of 2,2′-bithienyl (1.194 g, 7.18 mmol) in THF (75 mL) at −40 °C in an Ar atmosphere. The mixture was stirred at this temperature for 45 min at which time methyl iodide (1.45 mL, 23.0 mmol) was slowly added. It was stirred for a further 20 min and allowed to warm up to rt. After stirring at rt for 24 h, dilute HCl (10%) was added to the reaction mixture and the product was extracted with diethyl ether. The ether solution, washed with water, dried over Na_2SO_4, and filtered, was evaporated under reduced pressure to obtain a residue, which was charomatographed (silica gel) using *n*-hexane as eluant and then recrystallized from methanol to give 5,5′-dimethyl-2,2′-bithienyl (0.782 g, 56%): mp 64–6 °C (lit.[33] 64–5 °C); ^{1}H NMR δ 2.46 (d, 6 H, $J = 1.1$ Hz), 6.62 (m, 2 $H_{4,4'}$), 6.87 (d, 2 $H_{3,3'}$, $J = 3.55$ Hz); MS m/e 194 (100%, M^+), 179 (8%, $M^+ - CH_3$); UV (cyclohexane) λ_{max} nm (ϵ) 311 (14360).

5,5′-Di-*tert*-butyl-2,2′-bithienyl (3). $AlCl_3$ (1.0 g, 7.5 mmol) was added in one portion to a vigorously stirred solution of 2,2′-bithienyl (0.830 g, 5.0 mmol) and *tert*-butyl chloride (4.0 mL, 60 mmol) in CH_2Cl_2 (75 mL). The mixture was stirred for 24 h at rt in an anhydrous atmosphere and then poured into an excess of diluted HCl (10%). It was worked up as before and the residue was chromatographed (silica gel) using *n*-hexane as eluant and recrystallized from methanol to give 5,5′-di-*tert*-butyl-2,2′-bithienyl (1.053 g, 76%): mp 91–2 °C; ^{1}H NMR δ 6.89 (d, 2 $H_{3,3'}$, $J = 4.8$ Hz), 6.69 (d, 2 $H_{4,4'}$, $J = 4.8$ Hz), 1.38 (s, 18 H); UV (cyclohexane) λ_{max} nm (ϵ) 311 (15870). Anal. Calcd for $C_{16}H_{22}S_2$: C, 69.0; H, 8.0; S, 23.0. Found: C, 69.0; H, 8.1; S, 23.0.

5,5′-Bis(trimethylsilyl)-2,2′-bithienyl (4). 4 was prepared by the published procedure:[34] mp 89–90 °C (from methanol); ^{1}H NMR δ 7.22 (d, 2 $H_{3,3'}$, $J = 3.5$ Hz), 7.11 (d, 2 $H_{4,4'}$, $J = 3.5$ Hz), 0.34 (s, 18 H); MS m/z (%) 310 (90, M^+), 295 (100, $M^+ - CH_3$), 237 [2, $M^+ - Si(CH_3)_3$], 73 [44, $Si(CH_3)_3$]; UV (cyclohexane) λ_{max} nm (ϵ) 314 (19460). Anal. Calcd for $C_{14}H_{22}S_2Si_2$: C, 54.1; H, 7.1; S, 20.6. Found: C, 54.3; H, 7.2; S, 20.6.

2,2′-Bithienyl-3,3′-d_2. *n*-BuLi in hexane (1.4 M, 19.5 mL, 27.3 mmol) was added dropwise to a solution of 3,3′-dibromo-2,2′-bithienyl (4.09 g, 12.6 mmol) in THF (45 mL) at −80 °C in an Ar atmosphere. The mixture was stirred at this temperature for 30 min and allowed to warm up to rt. D_2O (3 mL) was added to the reaction mixture and stirring was continued for a further 15 min. The crude mixture was poured into an excess of water and extracted with $CHCl_3$. The organic solution, washed with water, dried over Na_2SO_4, and filtered, was evaporated under reduced pressure to give 2,2′-bithienyl-3,3′-d_2 (2.11 g, 100%): ^{1}H NMR δ 7.0 (d, 2 H, $J = 5.6$ Hz), 7.21 (d, 2 H, $J = 5.6$ Hz); exact/mass 168.003819 (calcd 168.003647).

5,5′-Bis(trimethylsilyl)-2,2′-bithienyl-3,3′-d_2 (8). *n*-BuLi in hexane (1.4 M, 8 mL, 11.2 mmol) was added dropwise to a stirred solution of 2,2′-bithienyl-3,3′-d_2 (0.559 g, 3.32 mmol) in anhydrous ether (20 mL) at rt in a rigorous Ar atmosphere. The mixture was refluxed (45 min) and allowed to cool to rt when chlorotrimethylsilane (1 mL) was added. Stirring at rt was continued (16 h). The crude was poured into an aqueous NaCl solution and extracted with ether. The organic solution, dried over Na_2SO_4 and filtered, was evaporated under reduced pressure and the residue in hexane was chromatographed (silica gel) and then recrystallized from methanol to give 5,5′-bis(trimethylsilyl)-2,2′-bithienyl-3,3′-d_2 (1.00 g, 96%): mp 90 °C; ^{1}H NMR δ 7.12 (s, 2 H), 0.32 (s, 18 H); exact mass 312.083412 (calcd 312.082705); m/e (%) 312 (76, M^+), 297 (100, $M^+ - CH_3$).

2- and 3-Isopropylthiophene. The mixture of 2- and 3-isopropylthiophenes were obtained according to the literature.[6] A solution of *i*-PrCl (9.35 g, 0.119 mol) and thiophene (10.0 g, 0.119 mol) in CH_2Cl_2 (32 mL) was added (45 min) at −70 °C to a suspension of $AlCl_3$ (16.53 g) in CH_2Cl_2 (25 mL). The mixture was stirred at this temperature for 1 h and then allowed to warm up to rt. After stirring at rt for 48 h and at reflux for 1 h, the reaction mixture was poured into ice–water, and the product was extracted with more CH_2Cl_2. The organic solution, washed with water and dried over Na_2SO_4, was chromatographed (silica gel) using CH_2Cl_2 as eluent, and the solution was evaporated under reduced pressure. Distillation of the oil gave a mixture of predominantly 2- and 3-isopropylthiophenes (12.31 g, 82.1%): bp 150 °C/760 mm; ^{1}H NMR δ 2.7–3.25 (m, 3 H), 6.6–7.3 (m, 1 H), 8.66 (d, 6 H, $J = 6.4$ Hz), 8.74 (d, 6 H, $J = 6.4$ Hz).

2-Iodo-5-isopropylthiophene (5) and 2-Iodo-3-isopropylthiophene (6). The isomeric mixture of iodoisopropylthio-

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phenes **5** and **6** was prepared according to a described procedure.[7] A mixture of 2- and 3-isopropylthiophenes (10.77 g), periodic acid (3.4 g), and iodine (8.66 g) in the solvent [$CH_3COOH–H_2O–H_2SO_4$ (100:20:3)] (50 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 $NaHSO_3$, then with aqueous Na_2CO_3 and with water, and evaporated at reduced pressure. Distillation of the oil (19.78 g) gave a mixture of 2-iodo-5-isopropylthiphene (**5**) and 2-iodo-3-isopropylthiophene (**6**) (17.12 g, 79.6%): bp 100 °C/0.6–0.7 mmHg; GC-MS 1st peak *m/e* 252 (57%, M^+), 237 (100%, $M^+ - CH_3$), 2nd peak *m/e* 252 (48%, M^+), 237 (100%, $M^+ - CH_3$); ^1H NMR isomer **6** δ 7.40 (dd, H_5, $J = 4.64$ Hz, $J' = 0.8$ Hz), 6.77 (d, H_4, $J = 4.64$ Hz), 2.8–3.55 (m, 1 H), 1.2 (d, 6 H, $J = 6.56$ Hz). Isomer **5** δ 7.03 (d, H_3, $J = 3.52$ Hz), 6.47 (dd, H_4, $J = 3.52$ Hz, $J' = 0.9$ Hz), 2.8–3.55 (m, 1 H), 1.3 (d, 6 H, $J = 6.56$ Hz). [Isomer ratio, **5**/**6**, 78:22].

5,5′-Diisopropyl-2,2′-bithienyl (2). **2** was prepared by a described procedure.[35] A mixture of iodoisopropylthiophenes (5.00 g, 19.85 mmol), $NiCl_2(PPh_3)_2$ (1.31 g, 2.0 mmol), Zn (1.95 g, 29.8 mmol), Et_4NI (5.11 g, 19.85 mmol), and THF (30 mL) was stirrèd at 50 °C in an inert atmosphere (Ar) for 2 h. The reaction mixture was poured into water and extracted with ether. The ethereal solution, washed with water and dried over Na_2SO_4, was evaporated and the residue purified by flash chromatography (silica gel; *n*-hexane) and then recrystallized twice, which gave 5,5′-diisopropyl-2,2′-bithienyl (0.169 g, 6.8%): ^1H NMR δ 6.90 (d, $H_{3,3'}$, $J = 3.2$ Hz), 6.67 (dd, $H_{4,4'}$, $J = 3.2$ Hz, $J = 0.8$ Hz), 2.85–3.35 (sep, 1 H, $J = 6.8$ Hz), 3.33 (d, 5 H, $J = 6.8$ Hz); exact mass 250.084499 (calcd for $C_{14}H_{18}S_2$: 250.084994). The mother liquours (1.198 g) contained a mixture in which more **2** (47%) was identified (HPLC).

Crystallographic Analysis of 1. Crystal and Intensity Data: $C_{10}H_{10}S_2$, $M_r = 194.32$, monoclinic unit cell, $a = 5.236(1)$, $b = 5.682(1)$, $c = 15.998(3)$ Å, $\beta = 92.27(1)°$, $V = 475.6(1)$ Å^3, space group $P2_1/n$, $Z = 2$, $D_x = 1.36$ g/cm^3, $\mu = 4.79$ cm^{-1}, $F(000) = 204$, 293 °K, crystal size: 0.4 × 0.5 × 0.09 mm, 962 reflections measured in the range $-6 \leq h \leq 6$, $0 \leq k \leq 6$, $0 \leq e \leq 18$ on an automated Enraf-Nonius four-circle diffractometer with graphite-monochromated Mo K_α radiation ($\lambda = 0.71069$ Å), 832 unique reflections from which 758 were observed ($I > 2.5\sigma(I)$). Three standard reflections monitored every 100 measurements had an intensity variation of 17.79%. Intensities were corrected for Lorentz, polarization, decay, and absorption effects (min and max transmission values: 78.3–99.1%). Final value of $R = 5.3\%$. **Structure Solution and Refinement.** The structure was solved by multisolution direct methods using the Ω-tangent formula[36] and refined by full-matrix least-squares procedures 8SHELX-76).[37] The hydrogen-atom positions were found from the difference Fourier map but were not refined. The non-H atoms were refined anisotropically (64 parameters, $w = 9.406/(\sigma^2(F) + 0.00167F^2)$, $R = 5.3\%$, $R_w = 5.2\%$, $S = 0.44$, $(s/\sigma)_{max} = 0.45$. Maximum and minimum height in final difference Fourier: 0.20 and −0.60 e Å^{-3}). The atomic scattering factors were taken from the *International Tables for Crystallography* and all calculations were performed on a VAX 4000 computer. The refined fractional atomic coordinates are available as supplementary material.

Crystallographic Analysis of 4. Crystal and Intensity Data: $C_{14}H_{22}S_2Si_2$, $M_r = 310.63$, monoclinic unit cell, $a = 6.521(4)$, $b = 15.878(1)$, $c = 8.987(3)$ Å, $\beta = 103.29(2)°$, $V = 905.6(6)$ Å^3, space group $P2_1/n$, $Z = 2$, $D_x = 1.14$ g/cm^3, $\mu = 3.63$ cm^{-1}, $F(000) = 332$, 293 °K, crystal size: 0.8 × 0.40 × 0.30 mm, 2308 reflections measured in the range $-8 \leq h \leq 8$, $0 \leq k \leq 21$, $0 \leq e \leq 11$ on an automated Enraf-Nonius four-circle diffractometer with graphite-monochromated Mo K_α radiation ($\lambda = 0.71069$ Å), 2180 unique reflections from which 1797 were observed ($I > 2.5\sigma(I)$). Three standard reflections monitored every 100 measurements had an intensity variation of 8.2%. Intensities were corrected for Lorentz, polarization, decay, and absorption effects (min and max transmission values: 97.1–99.3%). Final value of $R = 3.8\%$. **Structure Solution and Refinement.** The structure was solved by multisolution direct methods using the Ω-tangent formula[36] and refined by full-matrix least-squares procedures (SHELX-76).[37] The hydrogen-atom positions were found from the difference Fourier map but were not refined. The non-H atoms were refined anisotropically (84 parameters, $w = 1135/\sigma^2(F) + 0.000576F^2)$, $R = 3.82\%$, $R_w = 4.70\%$, $S = 0.52$, $(s/\sigma)_{max} = 0.6$. Maximum and minimum height in final difference Fourier: 0.34 and −0.26 e Å^{-3}). The atomic scattering factors were taken from the *International Tables for Crystallography* and all calculations were performed on a VAX 4000 computer. The refined fractional atomic coordinates are available as supplementary material.

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Supplementary Material Available: MINDO/3-optimized geometries for compound **1** and its radical cation $1^{•+}$ (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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