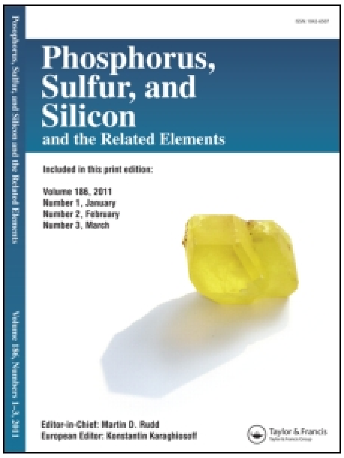

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RADICAL IONS 49[1] Redox Reactions of some Thiophene Derivatives

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RADICAL IONS 49[1]
Redox Reactions of some Thiophene Derivatives

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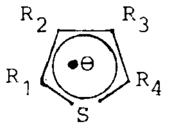
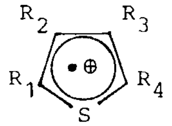
Trimethylsilyl- and cyano-substituted thiophenes can be reduced in THF using potassium and the resulting radical anions can be characterized by their electron spin resonance spectra. Attempts to oxidize thiophene derivatives with low first ionization potentials to their radical cations using the $AlCl_3/H_2CCl_2$ oxidizing system failed except for dithienyldisulfide, the radical cation of which rearranges under the reaction conditions to the one of dithieno[2,3-b,2′,3′-e]-*p*-dithiin. The photoelectron and electron spin resonance spectroscopic assignments are supported by MNDO as well as parametrized HMO calculations.

Trimethylsilyl- und Cyan-substituierte Thiophene lassen sich in THF mit Kalium reduzieren und die entstehenden Radikalanionen durch ihre Elektronenspinresonanz-Spektren charakterisieren. Versuche, Thiophen-Derivate mit niedriger erster Ionisierungsenergie duch Umsetzung mit $AlCl_3/H_2CCl_2$ zu ihren Radikalkationen zu oxidieren, blieben dagegen erfolglos. Eine Ausnahme ist Dithienyldisulfid, dessen Radikalkation sich unter Reaktionsbedingungen in das von Dithieno[2,3-b,2′,3′-e]-*p*-dithiin umlagert. Die Zuordnung der Photoelektronen- und der ESR-Spektren wurde durch Berechnungen nach MNDO- sowie parametrisierten HMO-Verfahren gestützt.

Radical ions of thiophene derivatives have attracted considerable interest over a long period of time; so far, the following mono-heterocyclic species have been characterized by ESR spectroscopy[3–11] (R_n other than H):



R_1 = $CN^{10)}$, $CHO^{5,7,8)}$, $C(O)CH_3{}^{5,7,8)}$, $NO_2{}^{4)}$
R_2 = $CHO^{5,7,8)}$, $NO_2{}^{4)}$
R_1 = R_4 = $CHO^{8)}$, $C(O)CH_3{}^{8)}$, $C(O)C(CH_3)_3{}^{8)}$, $C(O)CF_3{}^{8)}$, $NO_2{}^{4)}$ (1)
R_1 = NO_2; R_4 = $CH_3{}^{6,11)}$, $C_6H_5{}^{6,11)}$, $CN^{6,11)}$, $CHO^{6,11)}$, $COOCH_3{}^{6,11)}$, $SCH_3{}^{6,11)}$, $SO_2CH_3{}^{6,11)}$
R_1 = R_4 = CHO; R_1 = R_2 = $CH_3{}^{8)}$



R_1 = R_2 = $SCH_3{}^{9)}$
R_1 = R_2 = R_3 = R_4 = $C_6H_5{}^{3)}$, C_6H_4-$CH_3{}^{3)}$, C_6H_4-$Cl^{3)}$ (2)
R_1 = R_2 = SCH_3, R_3 = R_4 = $CH_3{}^{9)}$

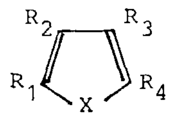
Obviously and expectedly, thiophene radical anions (1) are stabilized by electron withdrawing substituents R, whereas thiophene radical cations (2) are fewer in number with the positive charge partly delocalized into the groups R, which contain π systems or act as electron donors. As concerns the parent molecule, thiophene, the only ESR data available originate from solid state measurements of a radical species absorbed within a silicate structure containing $VO^{\oplus\oplus}$ or $Fe^{\oplus\oplus\oplus}$ ions.[12] Its g value is reported to be 2.0036, but no hyperfine structure could be detected. Considering these results and in order to enlarge the scope of thiophene radical ion stabilizing substituents, the following approach has been used to design novel $M^{\cdot\oplus}$ and $M^{\cdot\ominus}$ species:[13-15]

—For $M^{\cdot\oplus}$ generation, $AlCl_3$ in H_2CCl_2 proved to be an advantageous, oxygen-free and selective oxidizing system.[13]

—The oxidizability of compounds M to $M^{\cdot\oplus}$ can be tested by photoelectron spectroscopy (PES): in general, molecules M exhibiting a first vertical ionization potential below ~8 eV will undergo a one-electron transfer reaction with $AlCl_3/H_2CCl_2$.[13,14]

—Third-row element substituents like $-Si(CH_3)_3$[13,14] or $-SR$[13,15] proved to be stabilizing towards both radical ions $M^{\cdot\oplus}$ and $M^{\cdot\ominus}$ of the same molecule M.

Along these lines the thiophene and furane derivatives



$X = S,\ R_1 = R_4 = Si(CH_3)_3,\ CN$

$R_2 = R_3 = CN$ (3)

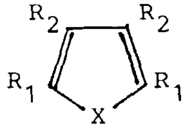
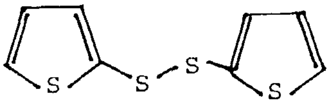
$R_1 = R_4 = Si(CH_3)_3,\ R_2 = R_3 = CH_3$

$X = O,\ R_1 = R_4 = Si(CH_3)_3$

as well as dithienyldisulfide have been synthesized and subjected to K/THF reduction and $AlCl_3/H_2CCl_2$ oxidation experiments.

TABLE 1

Vertical π ionization energies IE_1^v and IE_2^v(eV) of the thiophene and furane derivatives investigated as well as of some related compounds.

Compound	X	R_1	R_2	Ref.	IE_1	IE_2
	S	$Si(CH_3)_3$	H		8.20	8.81
	S	$Si(CH_3)_3$	CH_3		7.84	
	O	$Si(CH_3)_3$	H		8.12	(9.8)
	S	CN	H		9.76	10.59
	S	H	CN	17	10.20	10.45
	S	H	H	2	8.90	9.50
	S	CH_3	H	2	8.23	9.06
	S	H	CH_3	18	8.55	(8.85)
	O	H	H		8.88	10.31
					(8.4)	9.3

A. PHOTOELECTRON SPECTRA

The first two vertical ionization energies of all thiophene derivatives investigated are summarized in Table 1; the photoelectron (PE) spectra of 2,5-bis(trimethylsilyl)-thiophene and 2,2′-Dithienyldisulfide are displayed as examples in Figure 1. They will serve to illustrate, how the complex ionization patterns of compounds exhibiting numerous overlapping PE bands can be tentatively assigned.[16]

Advantageously, one starts from the well-established rule of thumb,[16] that within the He(I) ionization region only the np-type electrons of the elements and the 1s electron of hydrogen will contribute. Counting these electrons and dividing by 2 (Pauli's principle) yields the number of ionizations to be expected, i.e. for bis(tri-

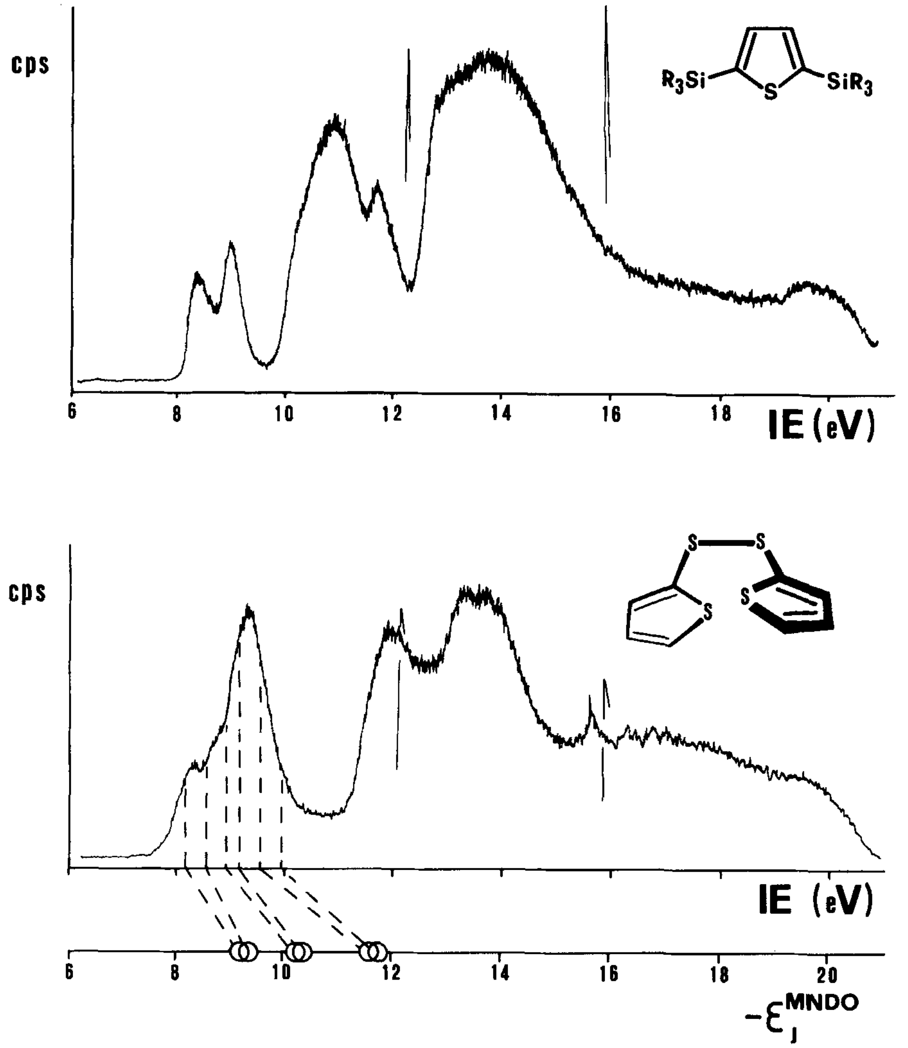
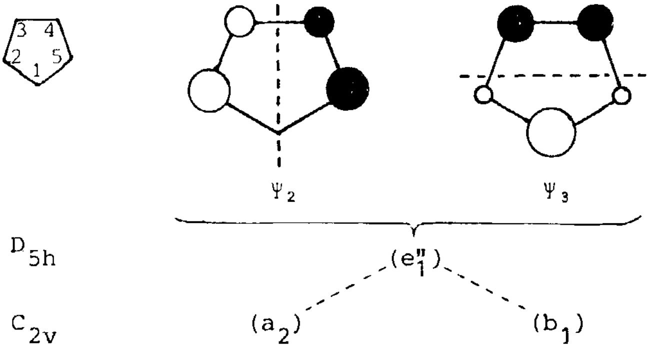


FIGURE 1 He(I)PE spectra of 2,4-bis(trimethylsilyl)thiophene and of 2,2′-dithienyldisulfide together with its assignment via KOOPMANS' correlation, $-\epsilon_J^{MNDO} = IE_n^v$.

methylsilyl)-thiophene, $C_{10}H_{20}Si_2S$, 24 PES bands are anticipated. Secondly, the PE spectrum (Figure 1) can be subdivided into 3 regions: The 2 separated peaks below 10 eV correspond to 2 of the 3 thiophene π-type ionizations. The broad hill between 10 eV and 12.5 eV comprises the third thiophene π ionization and the one of the in-plane sulfur lone pair as assigned for the parent thiophene molecule.[17] In addition, it contains the σ_{SiC} ionizations.[18] All other σ-skeletal ionizations are found at higher energies, predominantly under the huge ionization mountain between 12,5 eV and 16 eV.

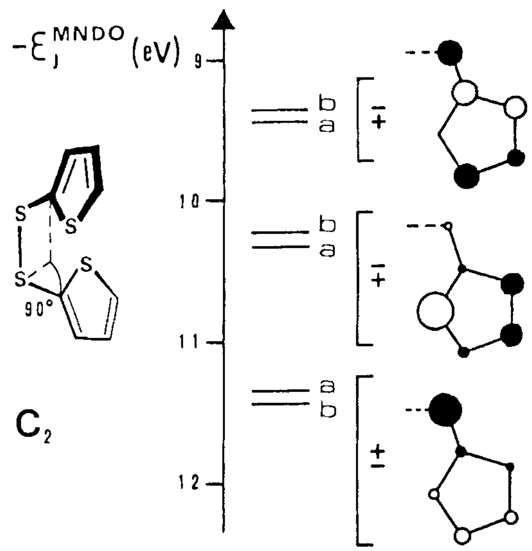
A corroboration of the above PES assignment for bis(trimethylsilyl)-thiophene can be based on qualitative perturbation arguments in discussing the substituent effects on the first two π radical cation states of the compounds listed in Table 1 starting from the highest occupied π orbitals of the cyclopentadienyl anion:[20]



(4)

S or O pertubation in position 1 will lower the b_1 orbital due to the higher effective nuclear charge of the heteroatoms. Electron donor (or acceptor) groups attached to the thiophene ring in 2,5- or 3,4- positions will raise (or lower, respectively) the orbitals differently: 2,5-substitution will shift a_2 more strongly than b_1; for 3,4-substitution a reverse perturbation is expected and found (Table 1: R = CN, CH_3). For simultaneous 2,5- and 3,4-substitution, the resulting shift is almost additive (Table 1, R = H, CH_3, $Si(CH_3)_3$). The trimethyl-silyl group exerts only a slightly larger effect than a methyl substituent. The furane π perturbation is comparable to that of thiophene (Table 1). The overall perturbation of cyanogen ligands comprises both inductive electron withdrawal and counteracting π delocalization.[21]

In the second PE spectrum displayed in Figure 1, i.e. in the one of 2,2′-dithienyldisulfide, 2 ionization regions each containing numerous overlapping bands will be distinguished: The smaller hill exhibiting a low-energy shoulder can be assumed to cover a total of 6 ionizations, which are assigned to the combinations of each the two thiophene π orbitals of a_2 and b_1 symmetry[17] as well as to the two p-type sulfur lone pairs of the disulfide bridge.[22,23] An MNDO calculation with full geometry optimization yields a dihedral angle $\omega(C_\alpha—S_1S_2—C_\alpha)$ ~90° together with only slight deviation from planarity, $\measuredangle(S_1—S_2C_\alpha—S)$ ~12°, within the two perpendicular thiophenedisulfide subunits. In the resulting C_2 symmetry, the 6 highest occupied MNDO orbitals show the following mixing:



(5)

Expectedly, of the original thiophene π orbitals the a_2 combinations interact strongly with the disulfide lone pairs, whereas the b_1 pairs are only minimally modified.[24] In order to determine the range of vertical ionization energies for the overlapping 6 PES bands, a Koopmans' regression based on the resolved π ionizations of thiophene,[17] its mono- and dimethyl derivatives,[23] of 1,2-dithiolane[25] and of dimethyldisulfide[22] has been calculated.

$$IE_n^v = -0.168 + 0.917\,(-\epsilon_J^{MNDO});\; SE = 0.34 \qquad (6)$$

Inserting the respective MNDO eigenvalues for dithienyldisulfide, the vertical ionizations assigned in Eq. (5) under the low energy PES band (Figure 1) should range from 8.41 eV to 10.3 eV in satisfying agreement with the observed band contour.

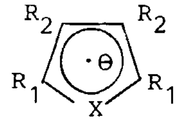
With respect to the potential one-electron oxidizability of the heterocycles investigated using the selective $AlCl_3/H_2CCl_2$ system,[13-15] the PE spectroscopic results can be summarized as follows: The required minimum value of the first vertical ionization energy of ≤ 8 eV[13] is exceeded by all thiophene and furane derivatives listed in Table 1, except for 2,5-bis(trimethylsilyl)-3,4-dimethyl-thiophene. This minimum value, however, rises to some extent if large structural changes stabilize the resulting radical cation during an adiabatic oxidation in solution e.g. by planarization of disulfide bridges[13,24-26] which considerably improves the large delocalization. Therefore, also 2,2'-dithienyl-disulfide, the PES low-energy flank of which reaches down to ~7,6 eV (Figure 1), has been reacted with the $AlCl_3/H_2CCl_2$ system.

B. ELECTRON SPIN RESONANCE SPECTRA

All thiophene and furane derivatives investigated here are reduced to the corresponding radical anions on bringing their THF solutions in contact with a potassium mirror (cf. Experimental Section). Their ESR data, summarized in Table 2, will be discussed first. The ESR spectra of both 2,5-bis(trimethylsilyl)-thiophene

TABLE 2

ESR coupling constants a_x (mT) and g values of the radical ions of thiophene and furane derivatives (in brackets: number of coupling nuclei)

Compound	X	R_1	R_2	a_H	a_{Si}	a_N	g
	S	SiR_3	H	0.194(2) 0.018(18)	0.386(2)	—	2.0047
	S	SiR_3	CH_3	0.15(6) 0.025(18)	[a]	—	[a]
	O	SiR_3	H	0.16(2) 0.04(18)	0.40(2)	—	2.0041
	S	CN	H	0.17(2)	—	0.17(2)	2.0049
	S	H	CN	[b]	—	0.450(2)	2.0036
 c)				0.236(2) 0.032(2)	—	—	2.0069

[a] Not determined.

[b] No assignment of the observed 2 triplets with $a_X = 0.677$ mT and 0.025 mT can be made (c.f. text).

[c] For the rearrangement to a dithiin derivative cf. text.

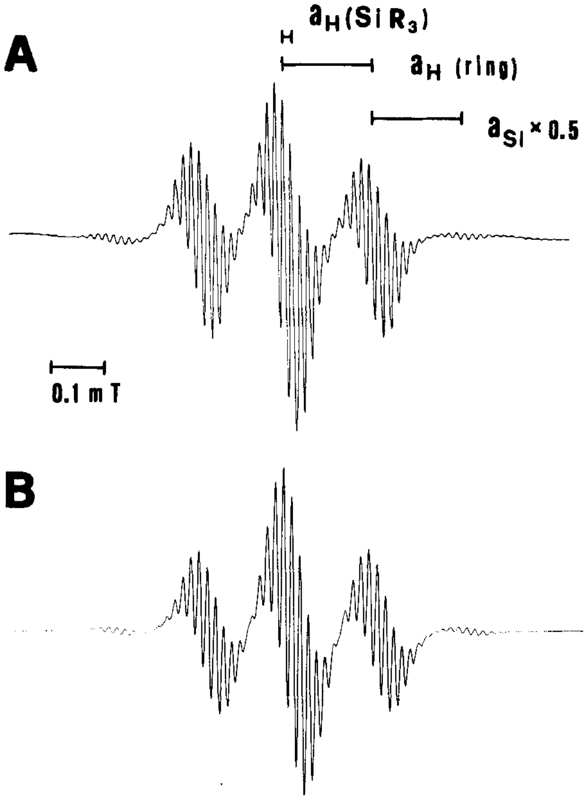


FIGURE 2 ESR spectrum of 2,5-bis(trimethylsilyl)thiophene radical anion at 180 K (A) and its computer simulation (B).

and -furane together with their perfect computer simulation are presented as examples in Figures 2 and 3.

In addition, the following comments are made on the generation of the individual radical ions and the interpretation of their ESR data (Table 2):

2,5-Bis(trimethylsilyl)thiophene Radical Anion

The species generated by potassium metal reduction at 200 K is stable up to 250 K. Its ESR spectrum is dominated by the large triplet due to the hydrogens at the 3,4-ring positions. Further hyperfine splitting is caused by the 18 equivalent hydrogens of the 2 trimethylsilyl groups (Figure 2:A). In addition, ^{29}Si satellites ($I(^{29}Si) = \frac{1}{2}$; 4.7% natural abundance) are noticeable as well-separated groups of lines. Starting from the experimental coupling constants (Table 2), a satisfactory computer simulation of the ESR spectrum is achieved (Figure 2:B).

2,5-Bis(trimethylsilyl)furane Radical Anion

Generation and properties are similar to those of the thiophene analogue. Its ESR spectrum (Figure 3:A), however, looks rather different due to the much larger coupling constant of the 18 equivalent methyl hydrogens. Because of the overlapping signals, the individual coupling constants (Table 2) had to be determined via insertion of approximated values to finally achieve the computer simulation of the ESR spectrum (Figure 3:B).

2,5-Bis(trimethylsilyl)-3,4-dimethyl-thiophene Radical Anion

The species found on contact with the potassium mirror at 200 K is stable only up to ~250 K. The ESR spectrum is dominated by the septet of the six equivalent hydro-

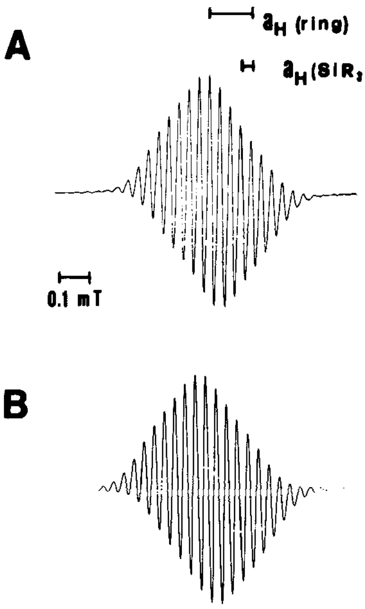


FIGURE 3 ESR spectrum of 2,5-bis(trimethylsilyl)furane radical anion at 180 K (A) and its computer simulation (B).

gens of the 2 methyl groups in 3,4-positions; further split by the signals of the 18 equivalent hydrogens of the 2 trimethylsilyl groups (Table 2). The assignment has been confirmed by perfect computer simulation. No ^{29}Si satellites could be observed, presumably due to the low signal-to-noise ratio.

2,5-Dicyanothiophene Radical Anion

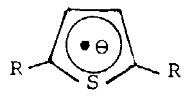
The potassium reduction at 200 K yielded a species $M^{\cdot\ominus}$ which is stable also at 300 K. Its ESR spectrum displays a septet of signals with rather large line-widths, which by computer simulation can be assigned to almost degenerate ^{1}H and ^{14}N coupling (Table 2). The *g* value observed is comparable to that of the trimethylsilyl-substituted thiophene radical anion, indicating considerable spin population at the sulfur center.

Potassium Reduction of 3,4-Dicyanothiophene

A radical anion stable up to room temperature is produced at 200 K. The $M^{\cdot\ominus}$ *g*-value measured is 2.0036; the ESR spectrum, however, shows not only the resolved ^{14}N quintet and a large ^{1}H triplet of 0.677 mT, but unexpectedly also an additional smaller triplet splitting of 0.025 mT and adequate intensity. An assignment to a dihydrothiophene radical anion formed by hydrogen transfer from the solvent can be discarded because dihydrothiophenes are known to be planar[27,28] and thus the hydrogens should be equivalent on the ESR time scale. Also an MNDO calculation with optimization of the structure predicts a planar configuration for a dihydrothiophene radical anion. If a dimer had been formed, the nitrogen coupling should have become a nonet. Altogether, the radical formed on potassium reduction of 3,4-dicyanothiophene remains undetermined.

Radical Anion Spin Populations

The ESR coupling constants observed for the $M^{\cdot\oplus}$ species generated (Table 2) compare well with literature values e.g. for 2,5-acceptor substituted thiophenes:[4,7]



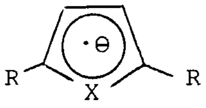
R	$-NO_2$	$-C(=O)CH_3$	$-C(=O)H$
a_H [mT]	0.133	0.146	0.152

(6)

Obviously, however, there appears to be no correlation to the acceptor strength, and especially the value observed for the trimethylsilyl derivative, $a_H = 0.194$ mT (Table 2), looks rather high. In order to elucidate the π spin population, HMO calculations have been performed incorporating the hyperconjugative effect of trimethylsilyl groups by introducing one (occupied) donor and one (empty) acceptor orbital at two centers connected to the 2,5-ring positions. The extensive HMO program[29] used starts from a set of literature perturbation parameters[20] as well as from additional experimental molecular state data such as PES π ionization energies and/or ESR coupling constants.[30] Using a gradient mode, the parameter set is optimized to the best fit of the experimental data, i.e. for the compounds discussed here by the following ones [in units β]:

$$\begin{array}{lll} h_S = 1.1; & k_{CS} = 0.75 & \\ h_O = 1.4; & k_{CO} = 1.0 & \\ h_{Si}^{D} = 1.6; & k_{CSi}^{D} = 0.4 & \\ h_{Si}^{A} = -1.7; & k_{CSi}^{A} = 0.15 & \\ h_N = 0.9; & k_{CN} = 1.9; & k_{C\text{-}CN} = 0.3 \end{array} \qquad (7)$$

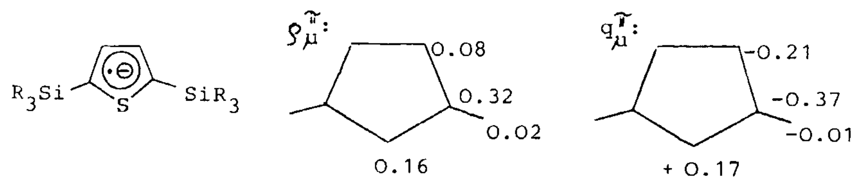
The calculated HMO quanities are actually reproducing the measured data e.g. based on the McConnell relation, $a_X^{\mathrm{calc.}} = |Q|\,(\ {}_{\mu}^{\mathrm{HMO}})^2$ with $|Q| = 2.55$ mT, the coupling constants:



X	R	$a_X^{\mathrm{calc.}}$	$a_X^{\mathrm{exp.}}$
S	SiR_3	0.196	0.194
O	SiR_3	0.160	0.16
S	CN	0.167	0.17

(8)

Therefore, the parametrized HMO wavefunction should also yield reliable information on π spin and π charge distributions, ρ_μ^π and q_μ^π, at the individual centers:



(9)

Both spin and negative charge are highest at ring π centers 2 and 5. According to the prediction (9), the trimethylsilyl group causes only weak perturbation, which agrees with the small ^{29}Si coupling constants (Table 2) observed.[13] The medium-sized g values of the thiophene radical anions (Table 2), therefore, are rather caused by the spin/orbit-coupling contributions of sulfur.[31]

$AlCl_3/H_2CCl_2$ Oxidation of 2,5-Bis(trimethylsilyl)-3,4-dimethylthiophene

Even at 200 K no ESR signal could be detected, although the oxygen-free and selective oxidation system chosen has been successful in generating numerous organosilicon radical cations[13] from compounds exhibiting first ionization potentials below 8 eV (cf. Table 1). Therefore, one has to assume that the resulting $M^{\bullet\oplus}$ species is not persistent,[32] i.e. kinetically unstable.

$AlCl_3/H_2CCl_2$ Oxidation of 2,2′-Dithienyldisulfide

Although this heterocyclic compound with a twisted SS bridge exhibits a first vertical ionization energy of ~8.4 eV (Table 1), its low-energy PES band tail reaches well beyond 8 eV (Figure 1). On contact with $AlCl_3/H_2CCl_2$ solution (cf. Experimental Section) a brown solution is readily formed at 200 K; the radical cation generated is stable up to room temperature and shows resolved ESR and ENDOR spectra (Figure 4).

The ESR spectrum (Figure 4:A) shows—besides signals from other radicals formed in the reaction mixture[24,33]—a triplet of triplets, the coupling constants of which can be read off directly from the ENDOR spectrum (Figure 4:B) to amount

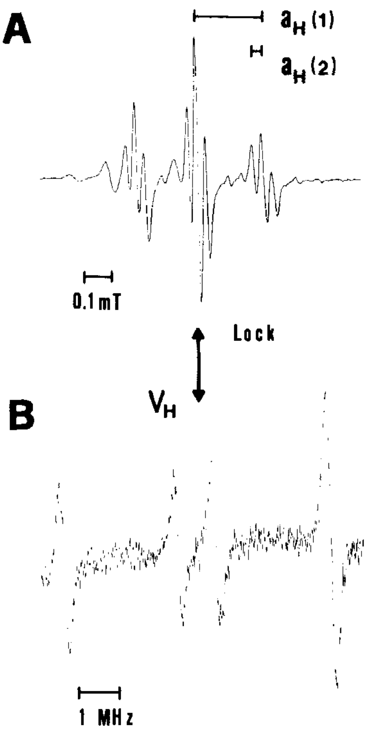
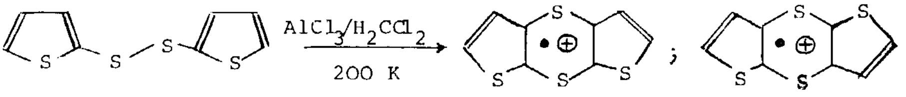


FIGURE 4 ESR (A) and ENDOR (B) spectra of the assumed dithieno[2,3-*b*;3′,2′/2′,3′-*e*]dithiine radical cations generated by $AlCl_3/H_2CCl_2$ treatment of 2,2′-dithienyldisulfide at 230 K.

to 0.236 mT (Table 2). In an obvious analogy to the oxidation of phenyldisulfides.[24,33] the assignment to one of the isomeric radical anions from dithieno[2,3-*b*;3′,2′,-*e*]- or [2,3-*b*;2′,3′-*e*]-*p*-dithiin is proposed following the rearrangement:



(10)

ESR assignment and the rearrangement (10)—proposed by analogy with previous results[24,33]—are strongly supported by the following arguments:

—The "cis" isomer has been synthesized[34,35] and characterized by X-ray structure analysis,[36] yielding a twist angle of 44° between the 2 thiophene planes.

—MNDO closed shell calculations show a minimum of the total energy at 27°, which in the radical cation should be lowered to 7° as predicted by an MNDO open shell geometry optimization—in analogy to the interpretation of experimental data of thiantrene radical cations.[37]

—Parametrized HMO calculations, with the parameter set (7) supplemented by k_{CS}(thiophene) = 0.65 and k_{CS}(dithiine) = 0.35, yield calculated hydrogen coupling constants, $a_H^{(1)} = 0.300$ mT and $a_H^{(2)} = 0.039$ mT respectively, in reasonable agreement with the experimental values (Table 2). For both the "cis" and "trans" isomers (10) identical coupling constants are predicted within the HMO approximation.

The 2,2′-dithienyldisulfide radical cation rearrangement provides another illustrative example[24,33] of how easily SS and also CS bonds are broken and restored to finally form the most stable radical cation accessible under the reaction conditions.

EXPERIMENTAL SECTION

Syntheses. Commercially available chemicals were used as starting materials without further purification except for thiophene and furane which were dried over $CaCl_2$ and distilled before use. All silylated compounds were prepared under dry nitrogen. THF was refluxed over metallic potassium and distilled. Dry quinoline was obtained by storage over KOH and subsequent distillation. Melting points are uncorrected. ^{1}H-NMR spectra were recorded using a VARIAN T-60 spectrometer; mass spectra using a VARIAN MAT CH 7 spectrometer.

2,5-Bis(trimethylsilyl)-thiophene:[38] To 70 ml of a 15% hexane solution of *n*-butyllithium (about 0.1 mole) 4.2g (0.05 mole) of thiophene in 30 ml THF were added at 0°C using a dropping funnel. The mixture was allowed to warm to room temperature until the butane development stopped. After cooling again to 0°C, 10.8g (0.1 mole) of trimethyl-chlorosilane were added. After refluxing for 1 hour, water was added. The organic phase was separated, dried and evaporated. The remaining oil crystallized on cooling. Despite repeated vacuum sublimation, the 1.1g (9.6%) product isolated was still only of crude quality: mp 27°C (lit. 30–31°C); ^{1}H-NMR ($CDCl_3$/TMS) $\delta = 0.30$ (18H), 7.09 (2H); MS mol peak at 228; analysis calc. for $C_{10}H_{20}SSi$ (228,5): C 52.56, H 8.82, S 14.03, Si 24.58; found C 47.8, H 8.1, S 13.75, Si 25.6.

2,5-Bis(trimethylsilyl)-furane:[39] The analogous procedure with 0.025 mole quantities yielded after vacuum distillation 0.33 g (10.6%) of an oil: ^{1}H NMR ($CDCl_3$/TMS) $\delta = 0.27$ (18H), 6.50 (2H); MS mole peak at 228.

2,5-Bis(trimethylsilyl)-3,4-dimethyl-thiophene:[40] The three-step synthesis starts from 2,3-dimethylbutadiene. 18 g (0.092 mole) Thiofluorenone (prepared according to[41]) were suspended in 230 ml petrol ether (bp. 60–70°C). After the addition of 10.9 g (0.133 mole) of 2,3-dimethyl-butadiene the mixture was stirred at room temperature for several hours. The colorless Diels/Alder-adduct was filtered off, washed with petrol ether and dried (yield: 19.4 g, 67%). Its pyrolysis in a 280°C metal bath gave 3 g (38%) of 3,4-dimethyl-thiophene, which was condensed in a cool-trap and purified by distillation: bp. 143–144°C; ^{1}H-NMR ($CDCl_3$/TMS) $\delta = 2.2$ (6H), 6.8 (2H); lit.[42] For final silylation, 1.5 g (0.013 mole) of 3,4-dimethylthiophene were refluxed 20 h after adding each 20 ml of ether and of a 15% *n*-buthyllithium haxane solution (0.035 mole). After cooling to 0°C, 3.5 g (0.032 mole) of trimethylchlorosilane were added and the reaction mixture refluxed for $\frac{1}{2}$ hour. The subsequent vacuum distillation (bp. 138–142°C, 14 Torr), yielded 0.9 g (27%) of a colorless oil: ^{1}H-NMR ($CDCl_3$/TMS) $\delta = 0.25$ (18H), 2.20 (6H); MS mol. peak at 256.

2,5- and 3,4-Dicyanothiophenes:[43] Are synthesized analogously starting from the corresponding 2,5-(ALDRICH) and 3,4-dibromo-thiophenes (prepared according to[44]): Each 4.84 g (0.02 mole) of the corresponding dibromothiophenes were refluxed with 5.2 g (0.058 mole) CuCN in 60 ml quinoline for 3.5 h. The reaction mixture was poured on ice and acidified with dilute HCl. The water phase as well as solid precipitates were extracted several times with ether. The ether phase was dried and evaporated; the residue recrystallized from chloroform and purified by vacuum sublimation. 2,5-Dicyanothiophene was isolated in 20% yield (0.5 g); mp. 103°C; MS mol. peak at 134; ^{1}H-NMR $\delta = 7.61$ ($CDCl_3$/TMS); analysis calc. for $C_6H_2N_2S$ (134,2) C 53.72, H 1.50, N 20.88, S 23.90; found C 53.4, H 1.7, N 20.85, S 23.6. 3,4-Dicyanothiophene was obtained starting from 0.005 mole in 7% yield (74 mg); mp. 172°C; MS mol. peak at 134; ^{1}H-NMR (acetone-d_6/TMS) $\delta = 7.70$.

2,2′-Dithienyldisulfide:[45,46] 82 ml 25% *n*-buthyllithium hexane solution (0.24 mole) were added to 11.5 g (0.137 mole) thiophene in 70 ml THF at −20°C to −30°C. After stirring for $\frac{1}{2}$ h, the mixture was cooled down to −70°C and 4.1 g elemental sulfur (0.128 mole) added in small portions. Stirred for another hour, the mixture was warmed to room temperature and poured into water containing ice. Acidification, ether extraction, evaporation and vacuum distillation yielded 7.5 g (47%) of thiophene-2-thiol as a yellow oil. 2.9 g (0.025 mole) of the thiol, 3.2 g of iodine (0.0125 mole I_2) and 2 ml (0.025 mole) of pyridine were refluxed in 50 ml of chloroform for $\frac{1}{2}$ hour. A brown residue of crude pyridine hydroiodide was filtered off, and the chloroform phase was washed with aqueous $Na_2S_2O_3$ solution until the color from unreacted iodine faded. Evaporation yielded an oil which solidified on standing and recrystallization from ethanol/H_2O 9:1, yielded 1.9 g (66%) of pale yellow crystal needles; mp 55°C (lit.[45,46] 56–57°C); ^{1}H-MNR: two unresolved multiplets at $\delta = 7.3$, 8.0, ratio approximately 2:1; analysis calc. for $C_8H_6S_4$ (230.4) C 41.71, H 2.63, found C 41.78, H 2.84; MS mol. peak at 230, fragment of mass 115.

Photoelectron Spectra were recorded on a PERKIN ELMER PS 16 spectrometer equipped with a heated inlet system. The $^2P_{3/2}$ peaks of Xe (12.13 eV) and Ar (15.76 eV) were used for calibration.

Radical Ions were generated and investigated in evacuated glass sample tubes with additional side chambers for inserting the compound as well as the purified solvent and redox reagents. All operations were carried out either under purified nitrogen or on the high-vacuum line, and the evacuated sample tube sealed off. Oxidation to radical cations was attempted with repeatedly sublimed $AlCl_3$ and degassed CH_2Cl_2 which had been stored over $AlCl_3$ in a trap connected to the vacuum-line and was condensed into the sample tube using a liquid nitrogen bath. After sealing off, the electron transfer reaction was started by thawing the frozen layers of H_2CCl_2 containing the compound and the $AlCl_3$ reagent at low temperature. Radical anions were prepared analogously, bringing into contact a potassium mirror distilled in vacuo with a cooled solution of the compound in THF, which had been degassed and stored over $LiAlH_4$ in the vacuum system.

ESR-Spectra were recorded using VARIAN E 9 or BRUKER 220 D spectrometers at 9.5 GHz/0.33 T. Perylene radical anion was used to calibrate coupling constants and to determine *g* values. The ENDOR spectrum was measured using the BRUKER 220 D spectrometer complemented by ENDOR equipment.

ESR Spectra Simulation was achieved on the DEC 10 computer at the Hochschulrechenzentrum Frankfurt using the program ESPLOT, a modified version of ESOP[47] kindly provided by Prof. A. v. Zelewsky, University of Fribourg.

MO Calculations: For MNDO calculations an adapted modified version of the original MNDO program[48] was available, kindly provided by Prof. M. J. S. Dewar, Austin, Texas. Both the semiempirical MO calculations and the HMO calculations based on molecular state parameters (introduced as specified in the text) were also carried out on the DEC 10 computer of the Hochschulrechenzentrum of the University of Frankfurt.

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REFERENCES

1. Part 48 cf. W. Kaim, P. Hänel, U. Lechner-Knoblauch and H. Bock, *Chem. Ber.*, **115**, 1265 (1982).
2. Part of the Ph.D. thesis B. Roth, University of Frankfurt 1982.
3. U. Schmidt, K. Kabitzke, K. Markau and A. Mueller, *Ann. Chem.*, **672**, 78 (1964).
4. E. A. C. Lucken, *J. Chem. Soc. A*, 991 (1966).
5. A. Hudson and J. W. E. Lewis, *Tetrahedron*, **26**, 4413 (1970).
6. A. S. Mukhtarov, V. I. Savir, A. V. Il'yasov and I. D. Morozova, Mater. Nauch. Konf. Inst. Org. Fiz. Khim., *Akad. Nauk. SSSR*, 85 CA **76**, 58474t (1970).
7. L. Lunazzi, A. Mangini, G. F. Pedulli and M. Tiecco, *Gazz. Chim. Ital.*, **101**, 10 (1971).
8. L. Lunazzi, G. F. Pedulli, M. Tiecco, C. Vincenzi and C. A. Veracini, *J. Chem. Soc. Perkin Trans. II*, 751 (1972).
9. C. M. Camaggi, L. Lunazzi and G. Placucci, *J. Chem. Soc. Perkin Trans. II*, 1491 (1973).
10. G. F. Pedulli, M. Tiecco, A. Alberti and G. Martelli, *J. Chem. Soc. Perkin Trans. II*, 1816 (1973).
11. C. M. Camaggi, K. Leardino and G. Placucci, *J. Chem. Soc. Perkin Trans. II*, 1195 (1974).
12. T. J. Pinnavaia, P. L. Hall, S. S. Cady and M. M. Mortland, *J. Phys. Chem.*, **78**, 994 (1974).
13. Cf. e.g. "Novel Radical Ions: Generation and Properties—An Interim Report on PES and ESR Investigation by the Frankfurt PES Group", H. Bock, G. Brähler, W. Kaim, M. Kira, B. Roth, A. Semkow, U. Stein and A. Tabatabai, in "Computational Methods in Chemistry", Plenum Press, New York 1980, or H. Bock and W. Kaim, *Acc. Chem. Res*, **15**, 9 (1982), and literature quoted.
14. Cf. e.g. H. Bock, G. Brähler, G. Fritz and E. Matern, *Angew. Chem.*, **88**, 765 (1976), *internat. Edit.*, **15**, 669 (1976), or *Z. anorg. allg. Chem.*, **439**, 173 (1978).
15. Cf. e.g. H. Bock and G. Brähler, *Angew. Chem.*, **89**, 893 (1977), *internat. Edit.*, **16**, 855 (1977), or *Chem. Ber.*, **112**, 3081 (1979).
16. H. Bock and B. G. Ramsey, *Angew. Chem.*, **85**, 773 (1973); *internat. Edit.*, **12**, 734 (1973).
17. P. A. Clark, R. Gleiter and E. Heilbronner, *Tetrahedron*, **29**, 3085 (1973).
18. P. Dechant, A. Schweig and U. Thiel, *Angew. Chem.*, **85**, 358 (1973); *internat. Edit.*, **12**, 308 (1973).
19. Cf. e.g. H. Bock, W. Kaim and M. Kira, *J. Organomet. Chem.*, **164**, 295 (1979).

20. Cf. e.g. E. Heilbronner and H. Bock "The HMO Model and its Application", Vol. 1, Wiley Interscience/Verlag Chemie, London 1976.
21. Cf. e.g. H. Stafast and H. Bock "Photoelectron Spectra of Cyanogen Compounds" in "The Chemistry of the Cyanogen Group" (Ed. S. Patai), Wiley/Interscience, London 1982.
22. Cf. e.g. G. Wagner and H. Bock, *Chem. Ber.*, **107,** 68 (1974) or. B. Solouki and H. Bock, *Inorg. Chem.*, **16,** 665 (1977) and literature quoted.
23. Cf. also the review by R. Gleiter and Spanget-Larsen, *Topics in Current Chem.*, **86,** 140 (1979) and references given therein.
24. J. Giordan and H. Bock, *Chem. Ber.*, **115,** 2548 (1982).
25. H. Bock, U. Stein and A. Semkow, *Chem. Ber.*, **113,** 3208 (1980) as well as H. Bock and U. Stein, *Angew. Chem.*, **92,** 863 (1980); *int. Ed.*, **19,** 834 (1980).
26. H. Bock, W. Schulz and U. Stein, *Chem. Ber.*, **114,** 2632 (1981).
27. T. Ueda and T. Shimanouchi, *J. Chem. Phys.*, **47,** 5018 (1967).
28. W. H. Green, *J. Chem. Phys.*, **49,** 177 (1968) and *Spectrochim. Acta A.*, **25,** 723 (1969).
29. Available for distribution.
30. Cf. e.g. P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37,** 2795 (1962) or G. F. Pedulli, M. Tiecco, A. Alberti and G. Martelli, *J. Chem. Soc. Perkin Trans. II,* 1816 (1973).
31. H. Bock, G. Brähler, D. Dauplaise and J. Meinwald, *Chem. Ber.*, **114,** 2629 (1981).
32. D. Griller and K.U. Ingold, *Acc. Chem. Res.*, **9,** 13 (1976).
33. H. Bock, U. Stein and P. Rittmeyer, *Angew. Chem.*, **94,** 540 (1982); *int. Ed.*, **21,** 533 (1982).
34. M. J. Janssen and J. Bos, *Angew. Chem.*, **81,** 257 (1969), *int. Ed.*, **8,** 272 (1969).
35. M. G. Woronkov and A. N. Pereferkowitsch, *Angew. Chem.*, **81,** 570 (1969), *int. Ed.*, **8,** 598 (1969).
36. H. Hiemstra and C. T. Kiers, *Acta Cryst.*, **B 35,** 1140 (1979).
37. Cf. e.g. P. D. Sullivan, *J. Am. Chem. Soc.*, **90,** 3618 (1968).
38. I. A. Konstantinov, Zh. Obshch, *Khim.*, **33,** 1251 (1963).
39. E. Lukevits, M. G. Voronkov, *Khim. Geterotsikl. Soedhin.*, **1,** 31 (1961).
40. C. Hoogsand, J. Nielsen and E. H. Braye, *J. Chem. Soc. D,* 1520 (1971).
41. "Methoden der Organischen Chemie (Houben-Weyl)", G. Thieme Verlag, Stuttgart 1955, 4th ed., Vol IX, p. 710.
42. B. König, J. Martens, K. Praefcke, A. Schoenberg, H. Schwarz and R. Zeisberg, *Chem. Ber.*, **107,** 2931 (1974).
43. C. Paulmier, J. Morel, P. Partour and D. Semard, *Bull. Soc. Chim. Fr.*, 2511 (1969).
44. S. Gronowitz, *Acta Chem. Scand.*, **13,** 1045 (1959).
45. "Organic Syntheses", J. Wiley and Sons, New York 1970, Vol 50, p. 104.
46. B. P. Fedorov and F. M. Stoyanovich, *Zh. Obshch. Khim.*, **33,** 2251 (1963); CA **59,** 13917g.
47. S. Richter, C. Daul and A. v. Zelewsky, *Inorg. Chem.*, **15,** 943 (1976).
48. M. J. S. Dewar and W. Thiel, *J. Amer. Chem. Soc.*, **99,** 4907 (1971).