Radical Cations and Anions from Some Simple Polythiophenes: an ESR Investigation

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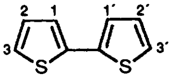
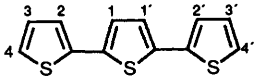
The radical cations and anions of the four lower oligomers of thiophene have been generated and characterized by means of ESR spectroscopy, with the exception of bi- and quinque-thienyl radical cations. *cis–trans* isomerism about the interannular bonds, similar to that previously reported for 2,2'-dithienyl radical anion, has been observed for terthienyl cation and anion radicals, while no direct evidence of such isomerism could be obtained for quaterthienyl and quinquethienyl.

In recent years, polythiophenes have been the subject of several chemical studies, most of which were concerned with a possible utilization of these compounds as organic conductors.[1] Among the many different kinds of polythiophenes, differing in the inter-ring bond positions, 2,5-polythiophenes represent perhaps the most interesting class, owing to their extended conjugated system. Although a relevant number of charged radicals from substituted thiophenes have been studied, little is known about radicals from simple polythiophenes. As to positively charged species, ESR studies have been carried out on the radical cations of thiophene[2] and thieno[3,2-*b*]thiophene,[3] as well as on those from some methyl substituted thiophenes.[4] Comparatively more investigations have been carried out on negatively charged thiophene derivatives: these included studies on dibenzothiophene,[5] [18]annulene-1,4;7,10;13,16-trisulphide,[6] [24]annulene-1,4;7,10;13,16;19,22-tetrasulphide,[7] 2,2'-dithienyl and 2-phenylthiophene,[8] some cyano-substituted thiophenes and thienothiophenes,[9] various benzodithiophenes[10] and 1,2-dithienylethylenes,[11] 2-(2-thienyl)thiazole,[12] 1,4-di(2-thienyl)benzene and 4-(2-thienyl)pyridine.[13]

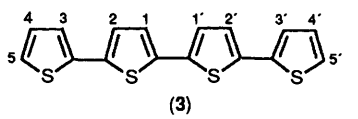
In order to obtain more information on the electronic properties of radical cations and anions of some thiophene oligomers, we have carried out an ESR investigation on the one-electron oxidation and one-electron reduction of four members of the 2,5-polythiophene family, *i.e.*, dithienyl (**1**), terthienyl (**2**), quaterthienyl (**3**), and quinquethienyl (**4**).



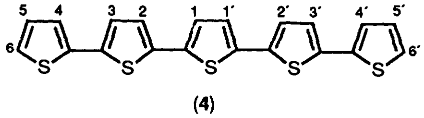
(**1**)



(**2**)



(**3**)



(**4**)

Results

Oxidation and Reduction of (**1**)–(**4**).—Oxidation of (**1**) in CH_2Cl_2/CF_3COOH (1:1) led to the observation of a weak ESR spectrum, characterized by a rather low *g*-factor, and indicating coupling of the unpaired electron with three pairs of equivalent protons (Table 1). The spectrum was slightly asymmetric and suggested the presence of more than one paramagnetic species; the second radical was however present in too small an amount to allow determination of its spectral parameters. In CH_2Cl_2/CF_3COOH (1:2) a different spectrum was obtained, showing coupling of the unpaired electron with five pairs of equivalent protons, which was identical with that observed by oxidation of quaterthienyl (**3**). The reduction of (**1**) has been previously investigated;[8] it leads to the radical anion which, under the chosen experimental conditions, exists in two conformations, that is the *cis* (**1a**) (*ca.* 20%) and *trans* (**1b**) (*ca.* 80%) (see Table 2).

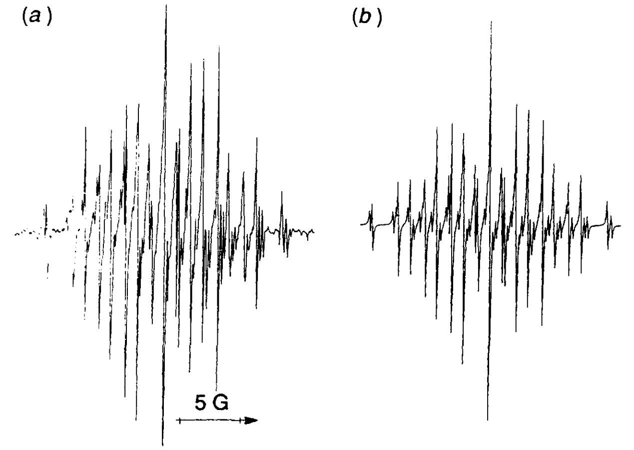


Figure 1. Experimental (*a*) and computer simulated (*b*) ESR spectra of the radical cation from terthienyl in methylene chloride at −40 °C.

Oxidation of (**2**) resulted in the detection of the strong and well resolved spectrum shown in Figure 1. The spectral pattern is the superimposition of the signals from two different radical species, having similar *g*-factors and slightly different hyperfine splitting (hfs) constants (see Table 1), which have been identified as two rotational isomers of $(\mathbf{2})^{+\bullet}$ (see discussion). From the spectra, it can be deduced that in the more abundant species (*ca.* 67%) the unpaired electron is coupled with three pairs of equivalent protons, while in the less abundant species (33%) couplings with six unequivalent protons can be resolved. Also the spectrum observed upon reduction of (**2**) at low temperature clearly indicates the presence of two radicals (see Figure 2). As in the case of $(\mathbf{2})^{+\bullet}$, the most abundant (*ca.* 67%) is fully symmetric, and indicates coupling of the unpaired electrons

Table 1. Experimental and calculated ($Q = -25$) hfs constants for radical cations from **(1)**–**(3)**.[a]

Cation	$a_{1.1'}$	$a_{2.2'}$	$a_{3.3'}$	$a_{4.4'}$	$a_{5.5'}$	g
(1)$^{+\cdot b}$	1.06 (2 H)	2.22 (2 H)	3.27 (2 H)			2.0024
(1)$^{+\cdot}$ (cal.)	−4.32	−0.19	−6.03			
(2b)$^{+\cdot}$ (67%)	2.18 (2 H)	3.20 (2 H)	<0.15 (2 H)	4.45 (2 H)		2.0025_9
(2c)$^{+\cdot}$ (33%)	1.97	3.22	<0.15	4.45		2.0025
	2.23	3.70	<0.15	4.65		
(2)$^{+\cdot}$ (cal.)	−2.29	−2.97	+0.17	−3.51		
(3)$^{+\cdot}$	2.82 (2 H)	0.98 (2 H)	2.38 (2 H)	0.22 (2 H)	2.64 (2 H)	2.0024_2
(3)$^{+\cdot}$ (cal.)	−2.47	−1.15	−2.01	+0.19	−2.23	

[a] Coupling constants in Gauss = 10^{-4} T; [b] Identity not ascertained.

Table 2. Experimental and calculated ($Q = -25$) hfs constants for radical anions from **(1)**–**(4)**.[a]

Anion	$a_{1.1'}$	$a_{2.2'}$	$a_{3.3'}$	$a_{4.4'}$	$a_{5.5'}$	$a_{6.6'}$	g
(1a)$^{-\cdot}$ (20%)[b]	3.97 (2 H)	0.70 (2 H)	4.80 (2 H)				—
(1b)$^{-\cdot}$ (80%)[b]	4.01 (2 H)	0.75 (2 H)	4.76 (2 H)				—
(1)$^{-\cdot}$ (cal.)	−3.42	+1.47	−4.88				
(2b)$^{+\cdot}$ (67%)	1.05 (2 H)	3.04 (2 H)	0.74 (2 H)	3.26 (2 H)			2.0043_5
(2c)$^{-\cdot}$ (33%)	1.05	2.89	0.72	3.28			2.0044_2
	1.05	2.97	0.72	3.56			
(2)$^{-\cdot}$ (cal.)	−0.32	−2.68	+0.95	−2.96			
(3)$^{-\cdot}$	1.96 (2 H)	0.27 (2 H)	2.21 (2 H)	0.51 (2 H)	2.21 (2 H)		2.0044_1
(3)$^{-\cdot}$ (cal.)	−1.05	+0.33	−1.92	+0.62	−1.95		
(4)$^{-\cdot}$	0.86 (2 H)	1.50 (2 H)	0.28 (2 H)	1.74 (2 H)	0.28 (2 H)	1.74 (2 H)	2.0041_0
(4)$^{-\cdot}$ (cal.)	−0.30	−1.12	+0.42	−1.38	+0.43	−1.35	

[a] Coupling constants in Gauss = 10^{-4} T; [b] Ref. 8.

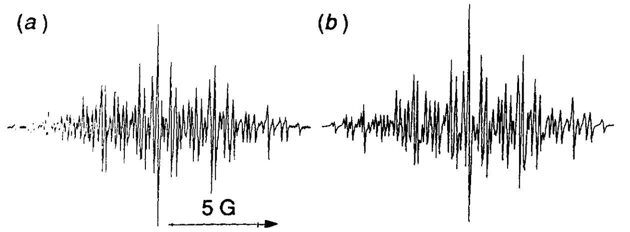


Figure 2. Experimental (*a*) and computer simulated (*b*) ESR spectra of the radical anion from terthienyl in THF at −70 °C.

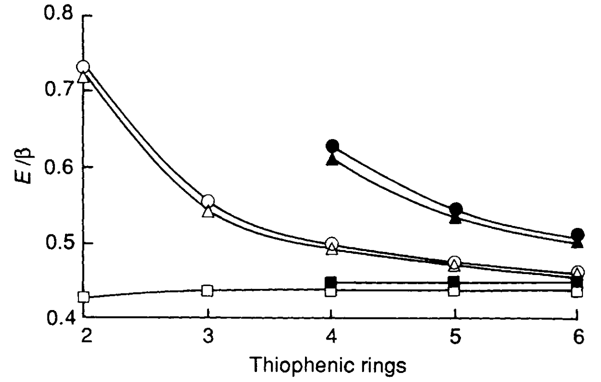


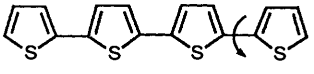
Figure 3. Calculated (McLachlan) energy barriers to rotation of the outermost (empty) and two outermost (full symbols) in polythiophenes (□, ■), their radical anions (△, ▲), and cations (○, ●).

with four pairs of equivalent hydrogen atoms, while the other (*ca.* 33%) shows couplings with four different and two pairs of equivalent protons (see Table 2).

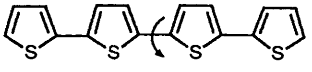
The spectrum obtained by oxidation of **(3)** is rather noisy and does not show any pronounced element of asymmetry. A satisfactory computer simulation can be obtained for a single species exhibiting coupling of the unpaired electron with five pairs of equivalent protons (see Table 1). Reduction of quaterthienyl at *ca.* −10 °C leads to a more or less symmetrical spectrum, characteristic of a single radical, the intensity of which decreases on either increasing or decreasing the temperature. Computer simulation was achieved by using the hfs constants given in Table 2.

Although several procedures were attempted, we did not succeed in generating the radical cation of quinquethienyl. On the other hand, reduction of **(4)** leads to the detection of a reasonably strong spectrum characterized by a symmetrical shape, indicating coupling of the unpaired electron with two pairs and two quadruplets of equivalent protons (Table 2).

MO Calculations.—MO calculations were carried out using the McLachlan procedure, and the computed coupling constants for the different radical cations and anions are listed in Tables 1 and 2 as appropriate. By performing calculations assuming a planar geometry of the molecules and by rotating out of the molecular plane the outermost or two outermost rings, we obtained an estimate of the barrier to ring rotation in the various compounds and radicals: calculations have been carried out also for sexithienyl for comparison purposes. The values, collected in Table 3 and shown graphically in Figure 3 in terms of the exchange integral β, indicate that in the diamagnetic molecules barriers to ring rotation are only marginally affected by the number of rings present. For the radical species, on the other hand, the barriers are always larger than those of the parent precursor: the actual values decrease significantly with increasing number of thiophene moieties and approach the value predicted for non-radical molecules. In compounds **(3)** and **(4)**, where rotation may take



(*a*) Rotation about an outer inter-annular bond (outermost ring);



(*b*) Rotation about an inner inter-annular bond (two outermost rings)

Table 3. Calculated energy barriers to the rotation of the outermost or two outermost rings in polythienyls and their radical cations and anions.[a]

Outermost ring				Two outermost rings		
Anion	Cation	Diamagn.	Compound	Anion	Cation	Diamagn.
0.719 76	0.730 86	0.428 94	(**1**)	—	—	—
0.544 35	0.555 55	0.438 30	(**2**)	—	—	—
0.494 01	0.499 58	0.439 48	(**3**)	0.609 41	0.626 18	0.448 83
0.472 21	0.475 39	0.439 70	(**4**)	0.537 26	0.546 01	0.450 22
0.460 91	0.462 94	0.439 74	Sexithienyl	0.504 16	0.509 37	0.450 48

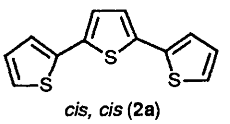
[a] Values expressed in β (exchange integral) units.

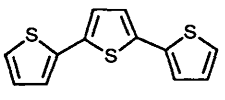
place around one of the inner or outer interannular bonds, as exemplified above for (**3**), the conformational barriers are predicted to be larger in the former than in the latter case.

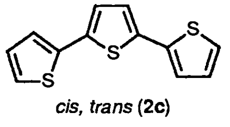
Discussion

Conformational Isomerism of the Radicals.—As mentioned in the preceding section, one electron oxidation of compounds (**1**)–(**3**) leads to the detection of paramagnetic species. Although the radicals obtained from compounds (**2**) and (**3**) can be identified as the corresponding radical cations on the basis of their spectral parameters, the nature of the species responsible for the spectrum observed upon oxidation of dithienyl (**1**) is dubious. The spectrum can, in fact, be interpreted in terms of coupling of the unpaired electron with three pairs of equivalent protons, but the measured hyperfine splittings (see Table 1) are much smaller than expected when compared with those available in the literature for the radical cations of thiophene and alkyl thiophenes, and with those of the higher oligomers (*vide infra*). Moreover, they are smaller than those predicted by McLachlan calculations, which, instead, satisfactorily reproduce those of the cations (**2**)$^{+\bullet}$ and (**3**)$^{+\bullet}$ and of the anions (**1**)$^{-\bullet}$ to (**4**)$^{-\bullet}$. Furthermore, while two conformers are observed for the radical anion (**1**)$^{-\bullet}$, *i.e.*, the *cis* and *trans* isomers in a 1:4 ratio,[8] the ESR spectrum obtained upon oxidation of (**1**) shows the presence of only one radical species. On the other hand, oxidation of (**1**) in the presence of an excess of trifluoroacetic acid leads to the spectrum of the radical cation of quaterthienyl, thus suggesting that the radical cation of dithienyl is indeed formed, but readily dimerizes under the experimental conditions. Occurrence of dimerization of these radical cations has already been observed in the course of electrochemical studies.[14]

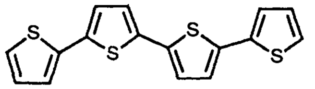
Oxidation and reduction of the trimer (**2**) lead in either case to the detection of two radical species in a 2:1 ratio (see Table 1 and 2), which we believe to be two of the three rotational isomers possible for this compound. Identification of the less abundant species with the *cis,trans* isomer for both the radical cation and anion appears straightforward when considering the non-equivalence of the hfs constants of the ring protons. The most abundant species, on the other hand, might in principle be either the *cis,cis* or the *trans,trans* isomer. On steric grounds, and by taking into account that the *trans* isomer is by far the more stable form for the radical anion of (**1**),[8] it seems reasonable to assign the *trans,trans* conformation to the dominant species. On a qualitative basis, by assuming that the relative weight of the *cis* and *trans* conformations about any inter-ring bond is the same found in the radical anion of 2,2′-dithienyl, *i.e.*, 1:4, and considering that of the three possible isomers of (**2**) the *cis,trans* is twice as probable as any of the other two, one may predict that the three isomers (**2b**), (**2c**), and (**2a**) should be present in a 16:8:1 ratio. The prediction is surprisingly good, when considering that the experimental *trans,trans*/*cis,trans* ratio was 2:1 for both the cation and anion radicals and that the amount of the *cis,cis* isomer is probably too small to allow detection. Assignment of the coupling constants to the different positions in (**2b**)$^{+\bullet}$ and (**2b**)$^{-\bullet}$ was based on the results of McLachlan MO calculations; in the case of the unsymmetrical (**2c**)$^{+\bullet}$ and (**2c**)$^{-\bullet}$ there are no elements for an unambiguous assignment to conformationally unequivalent protons.


cis, cis (**2a**)


trans, trans (**2b**)

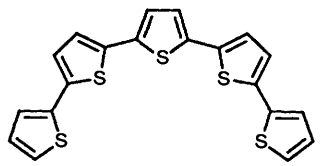

cis, trans (**2c**)

The presence of an additional thiophene ring in quaterthienyl increases the number of possible isomers to six, two of them being twofold. The relative amounts of the individual isomers predicted according to the aforementioned method would be 1 for *cis,cis,cis* (**3a**), 64 for *trans,trans,trans* (**3b**), 16 for *trans,cis,trans* (**2c**), 4 for *cis,trans,cis* (**3d**), 8 for *cis,cis,trans* (**3e**), and 32 for *trans,trans,cis* (**3f**), where the first four species should have four pairs of magnetically equivalent protons while the last two, owing to the absence of any symmetry element, should show unequivalent couplings to all the hydrogens. The ESR spectrum of (**3**)$^{+\bullet}$ is apparently consistent with the presence of a single radical characterized by five pairs of equivalent hydrogens (see Table 1), three of which have similar splittings in agreement with McLachlan calculations that predict couplings of *ca.* 2.5 G for the 1,1′, 3,3′, and 5,5′ positions. The observed isomer should be *trans,trans,trans* (**3b**)$^{+\bullet}$ by analogy with the lower oligomers. It is possible, however, that the ESR spectrum results from the superimposition of signals due to two or more isomers; the hfs constants of this cation being smaller than in the cation (**2**)$^{+\bullet}$, also the differences between the couplings of different isomers should also be smaller, thus making the separation of spectral lines due to the various species difficult. As a third possibility, a single time-averaged spectrum might be observed, since the increase of the number of rings leads to a reduction of the barrier to ring rotation (*vide infra*). Also, reduction of quaterthienyl leads to a symmetrical spectrum showing coupling of the unpaired electron with three pairs and a quadruplet of equivalent protons (see Table 2). This might be due to a single isomeric radical, or to fast rotational averaging, or, as stressed above for (**3**)$^{+\bullet}$, to the convolution of two or

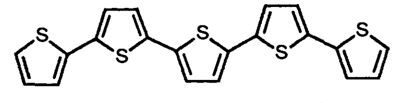

trans, trans, trans (**3b**)

more very similar spectra. The experimentally measured coupling constants are in very good agreement with the results of McLachlan calculations which predict practically identical couplings for the 3,3′ and 5,5′ pairs of hydrogens.

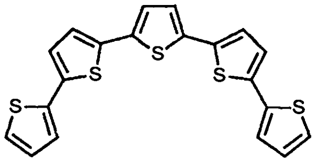
Compound **(4)** only afforded its radical anion; the spectrum was symmetrical, and a satisfactory simulation could be obtained by admitting coupling of the unpaired electron with the number (two pairs and two quadruplets) of equivalent hydrogen atoms expected on the basis of the structure of the starting compound. Due to the large number of thiophenic rings present, many rotational isomers may exist, four of which **(4a–d)** are characterized by six equivalent pairs of hydrogens. Also in this case it is impossible to tell whether the observed spectrum is due to a single species or results from the superimposition of two or more slightly different signals, or to time-averaging of the hyperfine splittings.



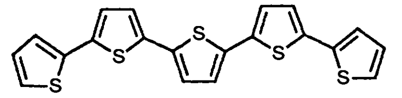
cis, cis, cis, cis, **(4a)**



trans, trans, trans, trans **(4b)**



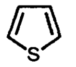
trans, cis, cis, trans **(4c)**



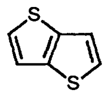
cis, trans, trans, cis **(4d)**

An examination of the data collected in Table 3 indicates that for both **(1)**$^{+\bullet}$ and **(1)**$^{-\bullet}$ the predicted rotational barriers are significantly larger than for dithienyl itself. It can also be seen that the increase in the number of rings leads to a substantial decrease in the rotational barriers in the radical species, the values of which get closer and closer to that of the parent molecules. The higher barriers predicted for the anions and cations originate from the fact that the LUMO of dithienyl has a bonding character between the atoms involved in the inter-ring bond. Introduction of an extra electron in that orbital (formation of the radical anion) will therefore enhance the rotational barrier. On the other hand, the HOMO of dithienyl is antibonding between those same atoms, and therefore the abstraction of an electron from that orbital (formation of the radical cation) will again produce an increase in the rotational barrier.[13] The presence of additional rings will extend the resonating system and reduce the height of the barriers in the radical species until, for an infinite number of rings, they will coincide with that of the corresponding diamagnetic compound. The barrier to ring-rotation in 2,2′-dithienyl is low as indicated by the observation of a single averaged NMR spectrum at room temperature; actually, the barrier to *s-cis,s-trans* interconversion in this compound has been calculated to be 4 kcal mol^{-1},[*,15] and an upper limit value of 5 ± 2 kcal mol^{-1} has been derived from an NMR study in liquid crystals.[16] The INDO computed barrier for **(1)**$^{-\bullet}$ is much higher, *i.e.*, 26.8 kcal mol^{-1},[13] and the *cis* and *trans* isomers were in fact experimentally detected. A comparison of these data with those collected in Table 3 suggests for **(2)**$^{+\bullet}$ and **(2)**$^{-\bullet}$, for which two isomeric forms are still observed, rotational barriers of as much as 15 kcal mol^{-1}. In the radicals from **(3)** and **(4)**, rotation about the outer rings might become fast enough to give time-averaging of the hyperfine splittings, owing to the small energy barriers which drop to levels significantly close to those of the parent molecules, while rotation about the inner interannular bonds should still be restricted. On this basis, it seems likely that the observation of a symmetrical spectrum is the consequence of the impossibility of resolving signals due to the different isomeric species.

Spin Density Distribution.—Previous studies on the radical cations of thiophene[2] **(5)** and some of its alkyl derivatives[4] have indicated that in these species the unpaired electron occupies a molecular orbital which receives only a minor contribution from the pertinent sulphur atomic orbital. This is evidenced by the rather large splittings exhibited by the hydrogens (or alkyl groups) bonded to the carbons adjacent to the sulphur atom (16 to 20 G) and by the small values of the *g*-factor (2.0020 to 2.0028). In fact, one may look at these systems as at substituted cyclopentadienyl radicals. In contrast, it has been argued that in the radical cation of thieno[3,2-*b*]-thiophene[3] **(6)** significant spin density is localized on the two heterocyclic sulphur atoms, to account for the rather small hyperfine coupling constants at the ring protons. Our results on the radical cations from polythiophenes **(2)** and **(3)** indicate that the spin distribution is analogous to that of thiophene radical cation. This situation is consistent with the results of McLachlan spin density calculations, which show that the singly occupied molecular orbital in the cations receives only a small contribution from the sulphur atoms.



(5)



(6)

The situation appears to be completely different for the radical anions of compounds **(1)**–**(4)**. In fact, all these species are characterized by *g*-factors in the range 2.0040 to 2.0045, which are significantly larger than those of the radical cations, and indicate participation of the sulphur atoms in the singly occupied MO. This is further substantiated by the fact that the positively charged radicals **(2)**$^{+\bullet}$ and **(3)**$^{+\bullet}$ exhibit an overall splitting larger than that of the corresponding anions. The finding that this trend is not maintained in the pair of radicals from **(1)** casts additional doubt upon the nature of the paramagnetic species observed upon its oxidation.

Experimental

Ter-,[17a] quater-,[17b] and quinque-thienyl[17c] were prepared according to described procedures, while, 2,2′-dithienyl (Aldrich) and all other chemicals were commercially available.

ESR Experiments.—Oxidation of **(1)** was achieved by addition of the compound (*ca.* 10^{-3} mol dm^{-3}) to a cold (*ca.* 0 °C) and oxygen-free mixture of methylene chloride and

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[*] 1 kcal mol^{-1} = 4.184 kJ mol^{-1}.

trifluoroacetic acid (1:1 in volume). No improvement of the signal-to-noise ratio was observed by photolysing the sample, but addition of a small amount of mercury(II) trifluoroacetate[18] resulted in a dramatic increase in the intensity of the ESR signal, and turned the colour of the solution from light blue to deep green. Use of mixtures of CH_2Cl_2/CF_3COOH (1:2) resulted in the detection of the radical cation of quaterthineyl, **(3)**$^{+\bullet}$. Under these conditions UV irradiation enhanced the intensity of the signal, this effect being accompanied by rapid sample depletion.

When terthienyl was dissolved (*ca.* 10^{-3} mol dm^{-3}) at low temperature in an oxygen-free mixture of CH_2Cl_2 and CF_3COOH (either 1:1 or 1:2 in volume) it gave a yellow–orange solution which exhibited no ESR signal. Addition of variable amounts of mercury(II) trifluoroacetate proved ineffective, as did irradiation with UV light. Oxidation of **(2)** could instead be achieved by adding aluminium trichloride to a degassed CH_2Cl_2 solution of **(2)** at −40 °C and by irradiating the sample with UV light. The spectrum intensity decreased slowly with time, and fell rapidly to undetectable levels if UV irradiation was interrupted. The radical cation of quaterthienyl was obtained by photolysing at *ca.* 0 °C a saturated solution of **(3)** in an oxygen-free CH_2Cl_2/CF_3COOH (1:2) mixture. The spectrum was, however, weak and did not improve by addition of mercury(II) trifluoroacetate.

Radical anions from compounds **(2)**–**(4)** were obtained by reducing the appropriate compound with sodium metal in carefully degassed tetrahydrofuran or 1,2-dimethoxyethane saturated solutions. The best operational temperature increased with increasing size of the substrate ranging from −50 °C for **(2)** to −10 °C for **(3)** and **(4)**. In the case of quinquethienyl, addition of some dibenzo-18-crown-6 ether proved critical for the observation of the ESR spectrum of the corresponding anion.

ESR spectra were recorded on a Bruker ER 200 D spectrometer, equipped with standard variable temperature devices. The magnetic field was calibrated with a NMR-gaussmeter, while *g*-factors were determined by means of a frequency counter and corrected with respect to that of the perylene radical cation. UV irradiation of the samples was achieved by focusing onto the spectrometer cavity the light of a 1 kW high pressure mercury lamp. A filter consisting of a water solution of $NiSO_4$ and $CoSO_4$ was used to eliminate the infrared component of the UV radiation.

McLachlan Spin Density Calculations.—Spin density distribution calculations were carried out according to the McLachlan method ($\lambda = 1.2$) using $h_S = 1.0$ and $k_{CS} = 0.86$.[19] In the calculations, dihedral angles of 0 (or 180) degrees between any two adjacent rings were assumed. For the determination of rotational barriers, calculations were also carried out assuming a 90° out-of-plane angle for the outermost or two outermost rings.

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