Electron paramagnetic resonance studies of electron attachment to thiophene, bi(thienyl) and some halogen-substituted thiophenes

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Exposure of dilute solutions of 2,2′-bithienyl in 2-methyltetrahydrofuran glasses at 77 K to ionizing radiation gave the corresponding radical-anion, as indicated by the EPR spectra. Similar treatment of thiophene solutions failed to give the expected π radical-anion, although electron capture clearly occurred: for CD_3OH and CD_3OD solutions the primary products were identified as the H- and D-atom-addition products, formed by protonation of the anions.

Under similar conditions, 2-bromothiophene gave clear EPR signals with features characteristic of the $C_{(2)}$–$^{\bullet}Br^-$ σ* radical-anion (with a spin density of ~37% on bromine). A σ* anion, with the unpaired electron localized in one of the C–Cl σ* orbitals, was detected following electron-addition to 2,5-dichlorothiophene, whereas for 2-chlorothiophene the corresponding σ* radical-anion, if formed, evidently decomposes rapidly to the 2-thienyl radical, whose EPR spectrum is reported. Only for 2,2′-bithienyl was the radical-anion's EPR spectrum detected in fluid solution following electron attachment.

These findings and the results of MO calculations are discussed in terms of the structures of the radical-anions and the alternative routes available for reaction following electron-addition.

Introduction

Many radical-anions of aromatic compounds, including, for example, $C_6H_6^{-\bullet}$ are relatively stable and have been thoroughly characterized by spectroscopic techniques, especially electron paramagnetic resonance (EPR) spectroscopy.[1] Hence it might be expected that radical-anions from thiophene and its simple derivatives would be sufficiently stable for detection and characterization; however, as far as we are aware the thiophene radical-anion itself has never been successfully studied. One aim of the present work was to investigate whether by generation at 77 K in solid matrices these radical-anions would prove to be sufficiently stable for detection and characterization using EPR spectroscopy. We also intended to investigate related species with extended conjugation (2,2′-bithienyl)[2] and halogen-substituted analogues (in irradiated 2-chlorothiophene crystals it is believed that the appropriate C–Cl σ* radical-anion, rather than the π* structure, is formed).[3] Attempts were also made to generate the appropriate radical-anions in fluid solution by one-electron reduction (with sodium or potassium) in an inert solvent [1,2-dimethoxyethane (DME)].

Experimental

EPR spectra were measured at 77 K using a Varian E109 X-band spectrometer. Samples, which were usually ~ 1 mol dm^{-3} in solute [methanol or 2-methyltetrahydrofuran (MTHF)] and frozen quickly in liquid nitrogen as small glassy beads, were exposed at 77 K to γ-rays from a ^{60}Co source, with doses between 10^3 and 10^4 Gy. Samples were annealed by decantation of the liquid nitrogen from the Dewar insert and allowing them to warm until significant changes were observed in the EPR spectra: they were then immediately recooled for measurement.

All substrates were commercially available, and used as obtained. The solvents employed were a 9:2 mixture (by volume) of CD_3OD and D_2O, a 9:2 mixture of CD_3OH and water, and MTHF (Lancaster Chemicals): the deuteriated alcohols (Aldrich) and D_2O (Goss Scientific) were used as supplied, and MTHF was distilled prior to use.

Thiophene derivatives were also subjected to treatment with sodium or potassium (typically as a freshly deposited mirror) in deoxygenated DME (concentration of substrate typically 10^{-3} mol dm^{-3}) at low temperature (~200 K) prior to recording of EPR spectra.

Simulations of anistropic EPR spectra were performed on a DEC VAX 3190 computer using programs written and provided by Professor P. H. Rieger and modified by Dr A. C. Whitwood to allow display and plotting of composite spectra from mixtures.

Results

Typical EPR spectra obtained from irradiated solid solutions of thiophene and its derivatives are shown in Figs. 1–4, and the data derived therefrom are shown in Table 1. For the CD_3OD spectra (see, *e.g.*, Fig. 2) the central features are due to a mixture of $^{\bullet}CD_2OD$ and $^{\bullet}CD_3$ radicals,[4] and free electrons trapped in the glass, and these conceal the central portion of the solute radical features. In some cases we were able to remove these signals by careful annealing (results not shown), but for some other systems where this was impossible we were nevertheless able to analyse the spectra satisfactorily on the basis of the outside lines. For the MTHF systems this was a greater problem because of the wide spread of solvent-derived radical signals but, again, careful annealing sometimes resulted in loss of these features prior to those from the solute radicals.

Discussion

Radical identification

(i) 2,2′-Bithienyl. Comparison of the quintet obtained from this substrate on electron-addition at 77 K (Fig. 1) with the

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Table 1 EPR parameters for radicals and radical-anions generated by electron-attachment to thiophene derivatives in solid matrices at 77 K[a]

Substrate	Solvent	Radical detected		EPR parameters (hfs/mT)	
2,2′-Bithienyl[b]	MTHF	**1**		0.4 (4 H)	$g \sim 2.00$
Thiophene[c]	CD_3OH	**2**	A_{xx}	3.3 (1 H) 1.2 (2) 3.1 (1 H) 0.1 (1)	g_{xx} 2.003
			A_{yy}	3.4 (1 H) 1.6 (2) 3.2 (1 H) 0.1 (1)	g_{yy} 2.009
			A_{zz}	3.2 (1 H) 1.0 (2) 3.0 (1 H) 0.1 (1)	g_{zz} 2.006
2-Bromothiophene	MTHF, CD_3OD	**4**	$A_{\parallel}$(Br)	42.0	g 2.00
			$A_{\perp}$(Br)	17.1	g 2.05
2,5-Dichlorothiophene	MTHF	**5**	$A_{\parallel}(^{35}Cl)$	8.1	$g \sim 2.00$
		9[d]	$A_{\parallel}(^{35}Cl) \simeq A(3\text{-}H)$	2.1	$g \sim 2.00$
2-Chlorothiophene	CD_3OD	**6**[d]	$A_{\parallel}$(2 H)[e]	2.0	$g \sim 2.00$

[a] In some cases after annealing; see text. [b] For details of isotropic spectra from radical **1** see text and ref. 2. [c] The g-values used were those for the 2-carboxy-5-hydro-4-thienyl radical (reported in ref. 4, p. 417. The z-axis (g-factor) was taken as perpendicular to the plane of the ring; the y-axis was taken as parallel to the plane of the ring in the direction of the bond between the carbon atoms in positions 3 and 4, with the x-axis mutually perpendicular to the y-axis. [d] On annealing. [e] Assigned to C3-H and C5-H, see text.

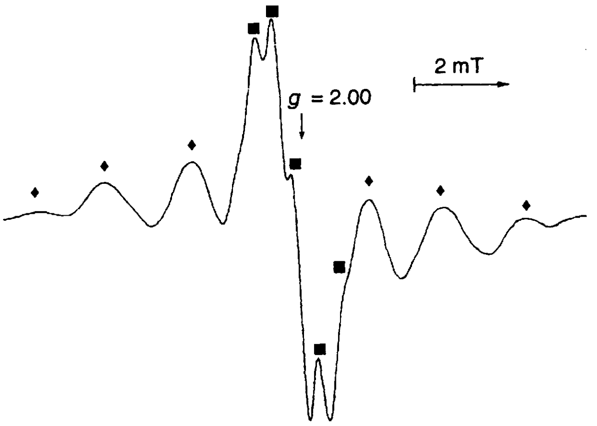


Fig. 1 EPR spectrum of the corresponding π* radical-anion from γ-irradiated 2,2′-bithienyl in MTHF at 77 K. ◆ Signals from the solvent. ■ Signals from the substrate.

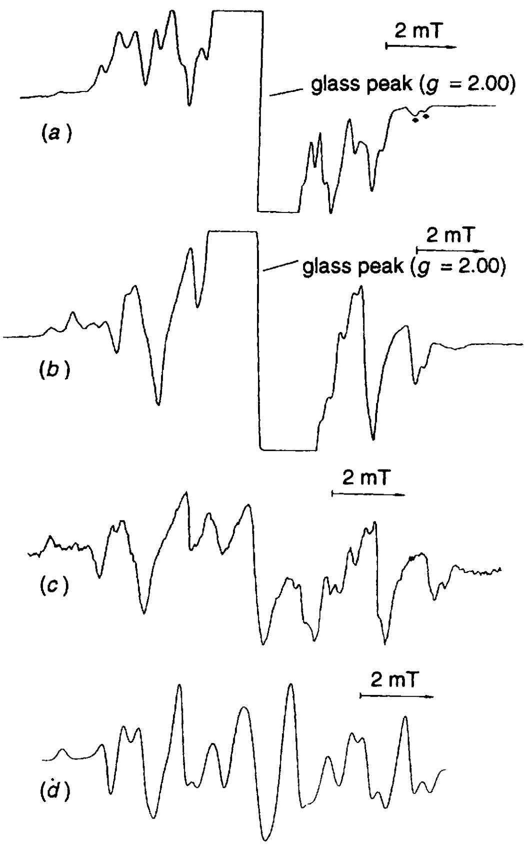
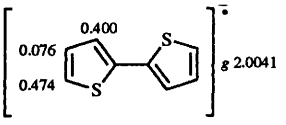


Fig. 2 (*a*) EPR spectrum from γ-irradiated thiophene in CD_3OD/D_2O at 77 K (the peaks marked ◆ are due to radicals obtained from HOD in the solvents. (*b*) EPR spectrum from γ-irradiated thiophene in CD_3OH–water at 77 K. (*c*) EPR spectrum from sample shown in Fig. 2(*b*) after annealing and refreezing twice. (*d*) Simulation of the spectra, shown in Figs. 2(*b*) and 2(*c*), attributed to 2-hydrothienyl (for parameters, see text and Table 1).

isotropic spectrum readily generated by one-electron reduction with sodium (*e.g.*, in DME at 210 K) clearly establishes that the spectrum is that of the (π*) radical-anion **1**. In fluid solution the high-resolution spectrum is dominated by signals from the *S-trans* rotamer with splittings and g-value as indicated (*cf.* ref. 2); the minor isomer (*S-cis*) has a(H) 0.477, 0.397 and 0.071 (g 2.0043).



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(ii) Thiophene. No feature that could reasonably be expected for the appropriate π* radical-anion could be detected in either solvent (a spectrum with nine lines and a total width of up to 3 mT would have been expected). However, for the CD_3OD solutions the spectra exhibit fairly well defined outer features and a total width of ~ 8.5 mT [see Fig. 2(*a*)]; use of CD_3OH led to the detection of a considerably wider spectrum (total width ~ 11 mT) with a triplet pattern (~ 1.2 mT) visible in the wings especially at high field [Fig. 2(*b*)]. The splittings are more clearly resolved in the spectrum [Fig. 2(*c*)] obtained after twice annealing and refreezing this sample; in the triplet (3.3 mT) of triplets (1.2 mT) observed, one of the former splittings evidently derives from the solvent (CD_3OH). Signals from the MTHF glass obscured any substrate-derived signals in this solvent.

We believe that the spectra in CD_3OD and CD_3OH shown in Fig. 2 are from the 2-hydrothienyl radical and its deuteriated counterpart **2**, in which a dominant splitting will be expected from the C^2–H(β) proton(s), with other splittings typical of an allyl radical moiety. The corresponding (protonated) radical has previously been detected[5] following irradiation both of a

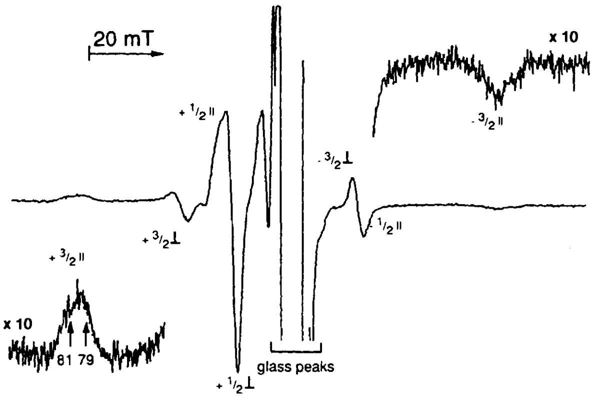
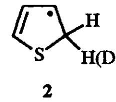


Fig. 3 EPR spectrum obtained from γ-irradiation of 2-bromothiophene in MTHF at 77 K, attributed to the σ* radical-anion

single crystal of thiophene and of thiophene adsorbed on silica gel. Spectral simulation with the anisotropic parameters shown in Table 1, including the introduction of anisotropic *g*-values and slight non-equivalence between the two β-protons, gave reasonable agreement with the observed spectra. The spectrum of the deuteriated analogue was similarly simulated, with substitution of the calculated value for *a*(D), satisfactory agreement again being obtained.



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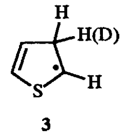

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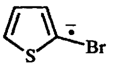
The formation of C-3 radical **2**, rather than C-2 radical **3**, is consistent with the rapid protonation (deuteronation) of the π* radical-anion by methanol at the site of highest negative charge density [as expected on the basis of molecular orbital (MO) calculations, using the PM3 Hamiltonian and restricted Hartree–Fock operator which leads to predicted values of ρ(π) of 0.13 (positions 2, 5) and 0.12 (positions 3 and 4)].

No EPR signals could be obtained in fluid solution in DME using either Na or K as reductant.

(iii) 2-Bromothiophene. The EPR spectrum obtained from this substrate in MTHF is shown in Fig. 3. This spectrum exhibits parallel and perpendicular features which are characteristic[6,7] of hyperfine coupling to bromine (see Table 1): the values observed ($A_{\parallel}$ 42.0 mT, $A_{\perp}$ 17.1 mT, $g_{\parallel}$ 2.00, $g_{\perp}$ 2.05) are similar to those obtained[6] for $C_6F_5Br^{\bullet -}$ and lead to an estimate[8] of 0.37 for the spin density on bromine in a σ* radical-ion **4**. No other signals could be obtained on annealing and refreezing. No signals could be obtained by reduction of this or the other halogeno-substituted thiophene derivatives in fluid solution with sodium or potassium.



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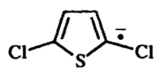

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(iv) 2,5-Dichlorothiophene. Irradiation of this substrate in MTHF at 77 K gave weak but well defined outer lines (see Fig. 4) assigned to the parallel features of a spectrum with a substantial *single* chlorine hyperfine splittings [$A_{\parallel}$ (^{35}Cl) 8.1 mT], which is characteristic of a σ* species with the unpaired electron localized in a single C–Cl bond:[3,6] the results are close to those obtained by Nagai and Gillbro[3] for the γ-irradiation of a single crystal of 2-chlorothiophene ($A_{\parallel}$ 8.4 mT), which strongly supports this conclusion [*cf.* also the value[6] of $A_{\parallel}$(^{35}Cl) 8.0 mT in $C_6H_5Cl^{\bullet -}$]. These features were lost on annealing: the resulting (weak) spectra showed a 1:2:2:2:1 pattern [*A* ~ 2.1 mT] discussed below.

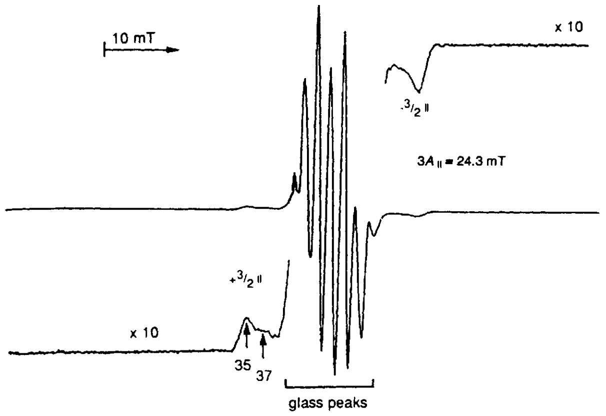
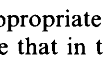


Fig. 4 EPR spectrum obtained from the γ-irradiation of 2,5-dichlorothiophene in MTHF at 77 K, attributed to the σ* radical-anion

(v) 2-Chlorothiophene. We failed to observe the corresponding σ* radical-ion in this case. Instead, at least in CD_3OD, a new species with large *g*-value variation and broad triplet splitting (~2.0 mT) was observed, these features being most easily distinguishable in spectra of samples which had been annealed and refrozen; no clear signals could be detected in MTHF. The spectrum was analysed in terms of the parameters given in Table 1 and was assigned to the 2-thienyl radical **6**, formed by loss of halide ion.



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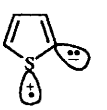
Whilst a splitting of ~2 mT is anticipated from the adjacent (*ortho*) proton in this σ radical (*cf.* the value for the phenyl radical)[9] the second splitting of this magnitude is unexpected: we believe that it derives from the hydrogen at C-5 in the thiophene ring and thus that significant spin density arises either *via* delocalization onto sulfur [*cf.* structure **7** or *via* interaction of the appropriate σ-orbitals across space (structure **8**)]. It is notable that in the σ* radical-anion from 2-chlorothiophene a substantial C^5–H splitting (0.75 mT) is also observed,[3] and that delocalization on to adjacent nitrogen in the related 2-pyridyl radical has also been reported.[10] The quintet observed in the spectrum obtained from 2,5-dichlorothiophene after annealing is similarly assigned to radical **9**, with *A*(3-H) ≃ $A_{\parallel}$(^{35}Cl) ≃ 2.1 mT.



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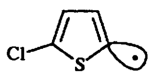

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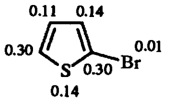
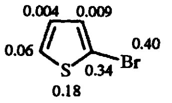
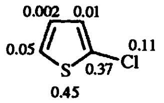
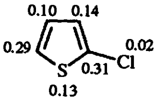
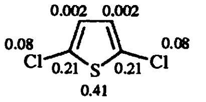
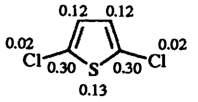
MO calculations

A limited range of MO calculations have been performed using the PM3 Hamiltonian in the MOPAC package; the results shown (Table 2) were obtained from restricted Hartree–Fock calculations on the neutral molecules (to avoid spin-contamination problems encountered in calculations of the thiophene and halogeno radical-anions themselves).

Table 2 Calculated energy levels and coefficient of LUMOs and adjacent higher energy orbitals of neutral halogenothiophenes

Compound	Orbital type	Σc_i^2	Energy/eV
2-Bromothiophene	π^* adjacent		−1.86
	σ^* LUMO		−2.05
2-Chlorothiophene	σ^* adjacent		−1.47
	π^* LUMO		−1.86
2,5-Dichlorothiophene	σ^* adjacent		−1.81
	π^* LUMO		−2.10

The calculated results for 2-bromothiophene are in good agreement with EPR findings: the calculated lowest unoccupied molecular orbital (LUMO) is a σ* orbital localized along the C–Br bond, with a small contribution from the sulfur atomic orbitals: the orbital of next higher energy is, as expected, the delocalized π* orbital, with little contribution from bromine atomic orbitals.

For the chlorine-substituted compounds, our calculational approach suggests that the π*, rather than the σ* (as observed), radical-anion is of lower energy. We believe, however, that the simplified calculational approach fails to allow for the stabilization which would result from a localization of the unpaired electron in the *stretched* C–Cl bond. Similarly, and not surprisingly, it fails to show that in the dichloro example the extra electron in the σ* orbital is located largely in a single σ* bond (as observed).

Conclusions

We conclude that the thiophene π* anion is a relatively strong base and that it is ring-protonated by methanol, even at 77 K. The parent anion is also probably formed in MTHF glasses, though the detection is prevented by the occurrence of intense solvent–radical features. In contrast, the σ* ($C-{}^{\bullet}Br^-$) radical-anion is favoured for the 2-bromo derivative. This is the precursor for dissociative electron capture which undoubtedly occurs readily in protic media. It is interesting that the 2,5-dichloro derivative gives a localized σ* radical-anion rather than a symmetrical delocalized centre. This illustrates well the concept that, on electron-capture, the C–Hal bond stretches because of the antibonding nature of the added electron; single bond stretch, rather than both simultaneously, is evidently preferred. Again, this σ* radical-anion is the precursor for the loss of halide ion.

Acknowledgements

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