An Electron Spin Resonance Study of the Radical Cations of Pyrroles, Furans, and Thiophenes in Liquid Solution

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Photolysis of alkylpyrroles in trifluoroacetic acid containing mercury(II) trifluoroacetate, alkylfurans in trifluoroacetic acid, or alkylthiophenes in sulphuric acid, induces oxidation to the corresponding radical cations. The e.s.r. spectra show that the electronic configuration is similar in all three species, the unpaired electron occupying the ψ_A MO in which the heteroatom lies in a nodal plane. Photolysis of 2,6-dimethyl- and 2,6-diethyl-thiophene in trifluoroacetic acid containing mercury(II) trifluoroacetate, on the other hand, gave rise to spectra with a high *g* value (2.0062), showing hyperfine coupling to two non-equivalent pairs of alkyl groups in an unsymmetrical dimer.

A variety of methods is now available for the one-electron oxidation of π-electron hydrocarbon systems in fluid solution, and by the application of these, the e.s.r. spectra of many types of simple alkenes, alkynes, and arenes have been recorded and rationalised.[1]

Relatively little work has been reported on the corresponding heteroarenes. We report here an e.s.r. study of the radical cations derived from three families of heterocyclopentadienes, namely the pyrroles, furans, and thiophenes, containing five π centres (**1**; X = NR, O, or S).

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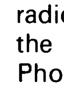

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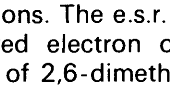

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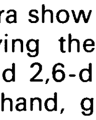

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Both the neutral cyclopentadienyl radicals (with five π centres),[2,3] and the cyclopentadiene radical cations (with four),[4–6] are relevant to this study.

The cyclopentadienyl radical (**2**) is orbitally degenerate between the ψ_A (**3**; X = CH) and ψ_s (**4**; X = CH) molecular orbitals, but the introduction of methyl groups can, in an additive manner, break the degeneracy. For example, 1,4-dimethylation preferentially destabilises ψ_A (**3**) by electron release, so that ψ_A makes the major contribution to the HOMO.[2,3]

The methylated cyclopentadiene radical cations $Me_nC_5H_{6-n}^{+\bullet}$ (**5**; *n* = 4—6) are generated when solutions of the parent hydrocarbons in trifluoroacetic acid are photolysed. The e.s.r. spectra show that the electron distribution in the SOMO of the diene is that shown in (**6**), which is similar to that in the ψ_A MO (**3**) of the cyclopentadienyl radical. Substituents at C(1) and C(4) show larger hyperfine coupling constants than those at C(2) and C(3), and substituents at C(5), which lie in the nodal plane, exhibit very little coupling.[4–6]

Studies have been reported by Symons,[7] and by Shiotani and Shida,[8] and their colleagues of the e.s.r. spectra of the radical cations (**1**; X = NR, O, or S), which were generated by γ-irradiation in Freon matrices. Spectra were obtained with a line width of a few gauss, and which showed that the electron distribution approximated to that shown in (**3**).

Results and Discussion

A variety of conditions was investigated for generating the pyrrole, furan, and thiophene radical cations ($\mathbf{1}^{+\bullet}$). E.s.r. spectra of good quality were obtained for the compounds listed in Tables 1 and 2.

The pyrrole radical cations could generally be generated by photolysing a solution of the substrate in trifluoroacetic acid containing mercury(II) trifluoroacetate (Kochi's reagent),[9] with light from a high-pressure mercury arc filtered through Pyrex glass.

The analyses of the spectra were confirmed by computer simulation. Examples of the spectra are shown in Figures 1 and 2.

Pyrrole itself in trifluoroacetic acid containing mercury trifluoroacetate showed only a singlet spectrum, *g* 2.0025, and a black solid separated from solution. This solid was washed and dried, when it still showed a singlet, *g* 2.0025, ΔH_{pp} 0.6 G.

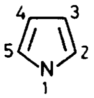
If alkyl groups were present in the 2- and 5-position no solid separated, and the e.s.r. spectra could be interpreted in terms of the simple monomeric radical cation.

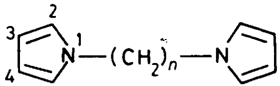
Hyperfine coupling constants varied little throughout the series, with *a*(Me-2,5) 15.50—16.08, *a*(H-3,4) 3.4—3.68, and *a*(N) 4.0—4.32 G. Proton hyperfine coupling to hydrogen or alkyl groups bonded to the nitrogen was never > 1.5 G, and any coupling to the phenyl protons in *N*-phenyl-2,5-dimethylpyrrole is < 0.1 G.

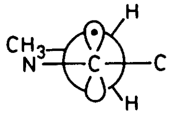
These values are in line with those obtained by Shiotani and Shida[8] for pyrrole, and by Symons[7] for pyrrole, *N*-methylpyrrole, and 2,5-dimethylpyrrole [*a*(2 Me) 17.5, *a*(2 H) 3.5, *a*(N) *ca.* 3 G in $CFCl_3$ at 77 K]. They are also in accord with the results of INDO calculations of spin densities and hyperfine coupling constants for the pyrrole radical cations.[8] The SOMO has the form shown in (**3**; X = NR).[7,8] The nitrogen lies in the nodal plane of the MO, and hyperfine coupling to nitrogen presumably originates principally through spin polarisation, and has a negative sign.

The methylene protons of ethyl groups in the 2- and 5-position show a larger hyperfine coupling constant (16.60—16.72 G) than those of methyl substituents (15.50—16.0 G), indicating that there is some preference for the conformation (**7**) where the C–C bond of the ethyl group lies in the nodal plane of the π-system. The temperature dependence of $a(CH_2)$ could not be determined because the trifluoroacetic acid solvent freezes at *ca.* −12 °C.

Table 1. Hyperfine coupling constants (G) and *g* values of pyrrole radical cations in trifluoroacetic acid at 283 ± 2 K



		Position						
		2,5		3,4	N		1	*g*
	Me	16.0 (6 H)	H	3.6 (2 H)	4.0	H	0.9 (1 H)	2.0026
	Me	16.0 (6 H)	H	3.4 (2 H)	4.2	Me	1.5 (3 H)	2.0026
	Me	15.44 (6 H)	Me	3.46 (6 H)	4.10	H	0.88 (1 H)	2.0029
	Et	16.72 (4 H)	H	3.44 (2 H)	4.32	Pr	0.90 (2 H)	2.0025
	Et	16.72 (4 H)	H	3.44 (2 H)	4.24	Bu	0.88 (2 H)	2.0024
	Et	16.60 (4 H)	H	3.66 (2 H)	4.00	Pr^i	0.70 (1 H)	2.0028
	Me	16.08 (6 H)	H	3.44 (2 H)	4.32	$PhCH_2$	0.96 (2 H)	2.0026
	Me	16.00 (6 H)	H	3.68 (2 H)	4.32	Ph	<0.1	
	Me	15.84 (6 H)	H	3.68 (2 H)	4.24	Pr^i	0.64 (2 H)	2.0027
								
$n = 2$	Me	16.24 (6 H)	H	3.44 (2 H)	4.40	CH_2	1.12 (2 H)	2.0025
$n = 2$	Et	16.48 (4 H)	H	3.44 (2 H)	4.23	CH_2	0.80 (2 H)	2.0024
$n = 3$	Me	16.00 (6 H)	H	3.62 (2 H)	4.40	CH_2	0.85 (2 H)	2.0025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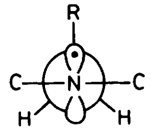
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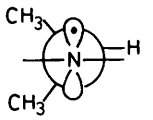
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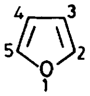
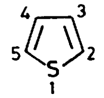
On the other hand, propyl, butyl, benzyl, or isopropyl substituents at nitrogen show smaller hyperfine coupling constants (0.64—0.96 G) than do the protons of a methyl group (1.5 G), suggesting that now the C–C bonds in the substituents lie out of the nodal plane [(**8**) and (**9**)].

Table 2. Hyperfine coupling constants (G) and *g* values of furan[a] and thiophene[b] radical cations



	Position			
	2,5		3,4	*g*
Me	16.6 (6 H)	H	3.6 (2 H)	2.0023
Me	16.2 (6 H)	Me	3.8 (2 H)	2.0021
Bu^t	0.6 (18 H)	H	3.8 (2 H)	2.0023
				
Me	17.0 (6 H)	H	3.1 (2 H)	2.0027
Et	19.5 (4 H)	H	3.2 (2 H)	
Bu^t	0.85 (18 H)	H	3.75 (2 H)	2.0019
Me	16.16 (6 H)	Me	3.45 (2 H)	2.0022

[a] In trifluoroacetic acid. [b] In sulphuric acid.

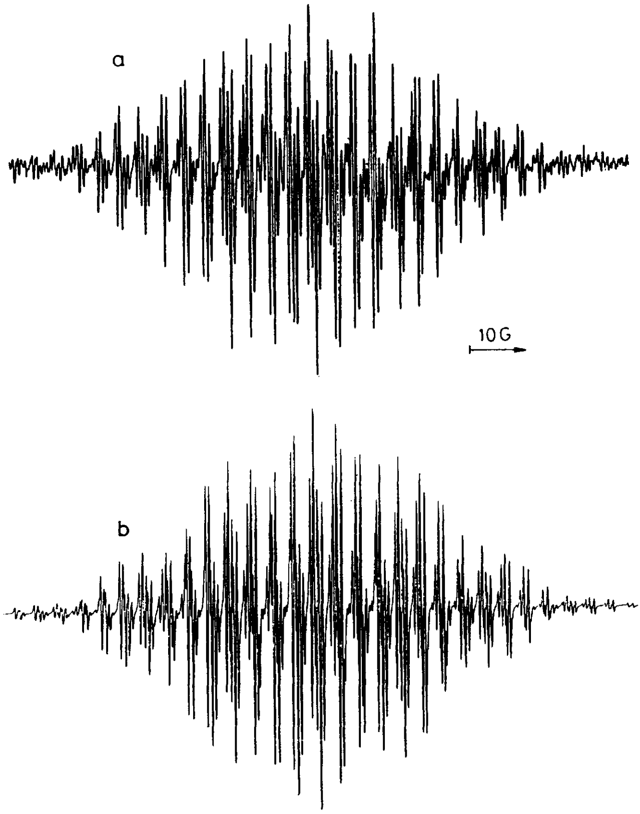


Figure 1. (a) E.s.r. spectrum of the 2,3,4,5-tetramethylpyrrole radical cation in trifluoroacetic acid at −12 °C. (b) Computer simulation

Many arene radical cations form complexes with their progenitors, $(Arene)_2^{+\bullet}$, in which the unpaired electron is equally shared between the two coparallel ring systems. In none of the above pyrrole radical cations did we find any evidence for the formation of such dimers.

In a recent interesting study Ohya-Nishiguchi showed that

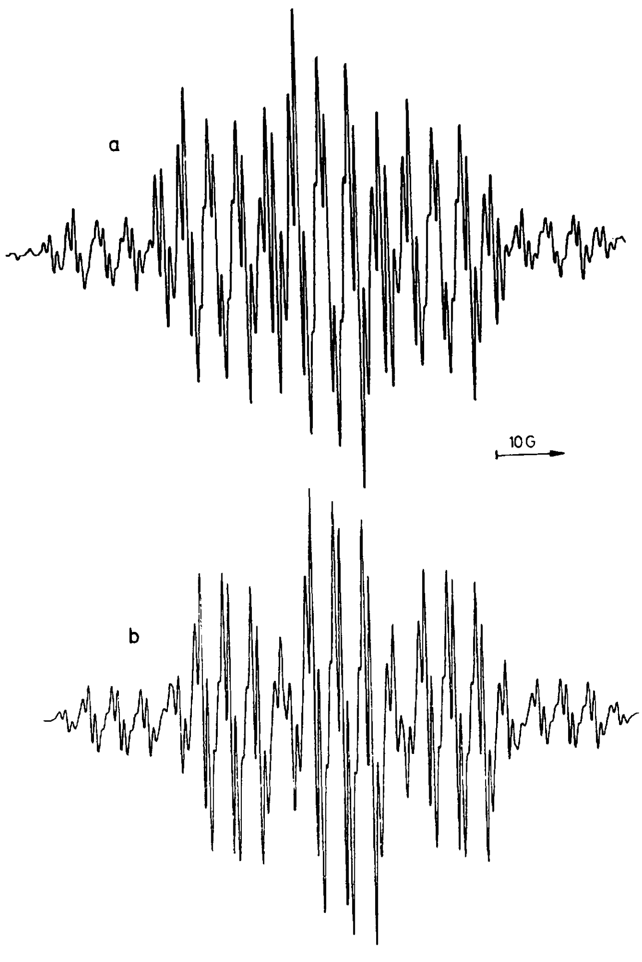
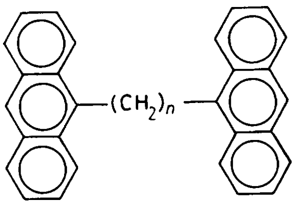


Figure 2. (a) E.s.r. spectrum of the *N*-butyl-2,5-diethylpyrrole radical cation in trifluoroacetic acid at −13 °C. (b) Computer simulation

dimer formation could be enhanced by connecting the two arene units by oligomethylene links of an appropriate length to permit the two arene units to lie coparallel.[10] Thus in the bi-9-anthracenyl derivatives (**10**), the unpaired electron was localised on one anthracene unit when n = 1, 2, or 4, but delocalised over both units when n = 3.



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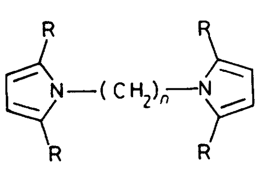

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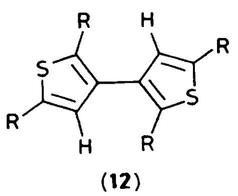

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In an attempt to encourage the interaction of the MOs between two pyrrole rings, we prepared the oligomethylene-dipyrroles (**11**; n = 2 or 3), and converted them into the corresponding radical cations. Rather surprisingly, when R = Me, n = 2, the cation could not be prepared using mercury(II) trifluoroacetate in trifluoroacetic acid, but a good e.s.r. spectrum was obtained when thallium(III) trifluoroacetate was used as the reagent. The spectra showed that in all three compounds, the unpaired electron was localised in one ring.

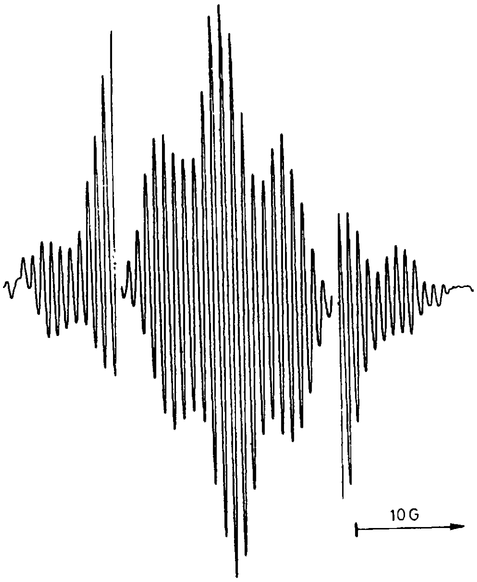

Figure 3. E.s.r. spectrum of 2,5-di-t-butylfuran in trifluoroacetic acid at −12 °C. ^{13}C Satellites are shown in the inset

The e.s.r. spectrum of the ethyl derivative (**11**; R = Et, n = 2) showed a strong alternating linewidth effect in the CH_2Me quintet, indicating a barrier to rotation about the C–CH_2Me bond, with a minimum of energy apparently where the methyl group is directed towards the heteroatom, as shown in (**7**).

The furan radical cations listed in Table 2 can be formed merely by photolysis of the substrates in trifluoroacetic acid. The spectrum of 2,5-di-t-butylfuran is illustrated in Figure 3; that of the 1,2,3,4-tetramethyl derivative was shown in our preliminary note.[11] We have used a similar technique for generating other types of radical cations, particularly the methylcyclopentadiene radical cations, where there was evidence that the reaction involved homolysis of the protonated cyclopentadiene.[6]

The proton hyperfine coupling constants to methyl at the 2- and 5-position, or hydrogen or methyl at the 3- and 4-position, are similar to the corresponding values in the pyrroles, in accord with the Freon matrix studies by Symons on furan, and by Shiotani and Shida on furan, 2-methylfuran, and 2,5-dimethylfuran [for which they report a(6 H) 16.9, a (2 H) 4.3 G].

This confirms that the SOMO is again ψ_A (**3**) as it is in pyrroles, in conformity with INDO calculations,[8] and with results from photoelectron spectroscopy,[12] which place ψ_A above ψ_s in energy.

Shiotani and Shida reported the formation of the furan dimer radical cation in a Freon matrix,[8] but again we were not able to observe the spectra of any dimer radical cations from our alkylated furans.

When thiophene itself was photolysed in trifluoroacetic acid containing thallium(III) trifluoroacetate, the solution showed a strong singlet spectrum, g 2.0034, and a black solid separated. This solid was collected and dried, when it still showed a strong spectrum, g 2.0034, ΔH_{pp} 1.45 G.

Photolysis of the other thiophenes in sulphuric acid solution

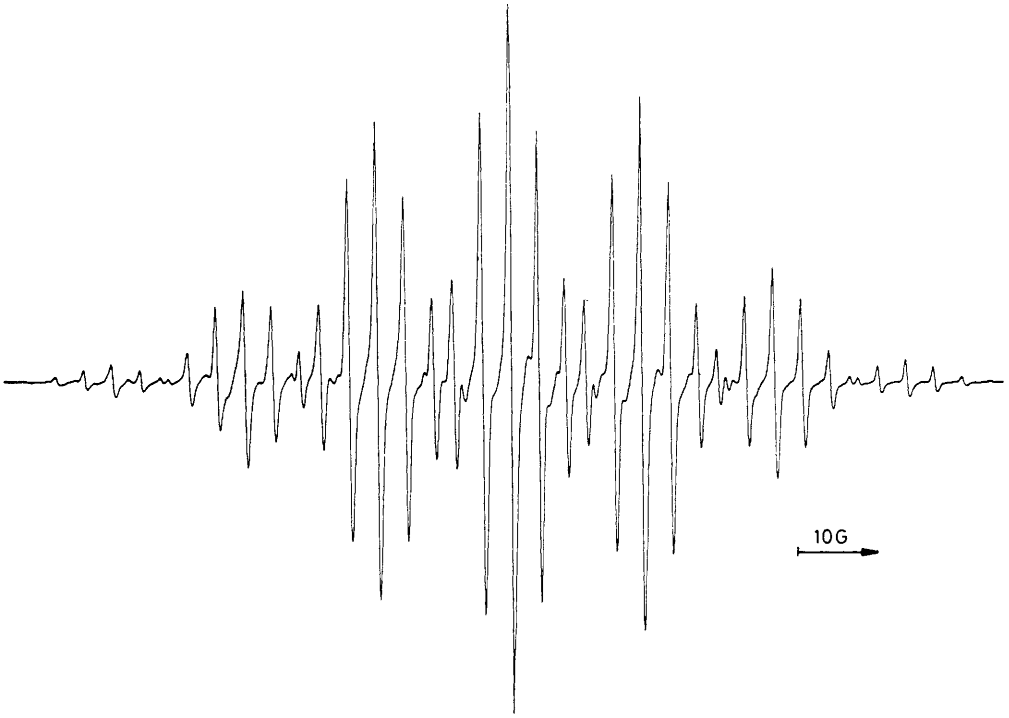

Figure 4. E.s.r. spectrum of the 2,3,4,5-tetramethylthiophene radical cation in trifluoroacetic acid at −13 °C

gave rise to spectra of the corresponding radical cations; the spectra obtained from 2,5-dimethyl-, 2,5-di-t-butyl-, and 2,3,4,5-tetramethylthiophene (Figure 4) were strong and well resolved, but that from 2,5-diethylthiophene was weak.

Again the hyperfine coupling constants [Table 2: *e.g.* 2,5-$Me_2C_4H_2S^{+\bullet}$, a(2 Me) 16.6, a(2 H) 3.8 G] are similar to those in the corresponding pyrrole and furan radical cations, and are in accord with the values obtained from experiments on Freon matrices [*e.g.* 2,5-$Me_2C_4H_2S^{+\bullet}$, a(2 Me) 18.1, a(2 H) 3.5 G at 77 K] and from INDO calculations.[8] Again the SOMO is the ψ_A orbital, with the heteroatom lying on the nodal plane.[7,8]

Different behaviour was observed when radical cations were generated from thiophenes under other conditions.

When 2,5-dimethylthiophene was dissolved in trifluoroacetic acid, or dichloromethane containing mercury(II) trifluoroacetate, photolysis with Pyrex-filtered u.v. light gave rise to a strong spectrum with a high g value (2.0064) consisting of a setptet of septets (Figure 5), a(6 H) 4.9, a(6 H) 2.1 G. Similarly 2,5-diethylthiophene in trifluoroacetic showed a quintet of quintets, a(4 H) 5.0, a(4 H) 2.15 G, g 2.0064.

These results imply the formation of an unsymmetrical dimer, different from the symmetrical dimers which are formed from R_2S radical cations ($R_2SSR_2^{+\bullet}$) or from arenes. One possible structure for the dimer is shown in (**12**). This would be equivalent to the formation of the biphenyl radical cation from benzene,[13] but if it is correct it is surprising that no coupling can be detected to the protons on the ring.

In attempts to obtain information on the structure of the dimer, a solution of 2,5-dimethylthiophene in trifluoroacetic acid was photolysed, then quenched with water, but the mass spectrum of the product showed the presence principally of a trimer, M 336.

Similarly 2,5-di-t-butylthiophene in sulphuric acid showed the spectrum of the monomeric radical cation, a(2 H) 3.75, $a(Bu^t)$ 0.85 G, but in trifluoroacetic acid in the dark it gave rise to a strong singlet, g 2.0055. On photolysis, this left a small amount of the singlet, and gave rise to multiplet of at least 19 lines, a *ca.* 0.80 G, ΔH_{pp} 0.30 G, g 2.0020.

With thallium trifluoroacetate in trifluoroacetic acid, the same di-t-butylthiophene gave in the dark what appeared to be a singlet at g 2.0067 and a weaker one at g 2.0056. On photolysis, this left the singlet at 2.0067 which now showed multiplet coupling at *ca.* 0.17 G, and gave rise to a multiplet of at least 19 lines, a 0.78 G, ΔH_{pp} *ca.* 0.3 G, g 2.0020 (Figure 6).

The partially resolved signal with g 2.0067 may relate to a dimer similar to that which we obtained from 2,6-dimethyl- and 2,6-diethyl-thiophene. The low g value (2.0020) of the multiplet which is produced on photolysis appears more characteristic of a monomer. One possible candidate might be 2,3,4,5-$Bu^t_4C_4S^{+\bullet}$, formed by acid-catalysed transalkylation.

Photolysis of a solution in trifluoroacetic acid, or in dichloromethane with aluminium chloride, of a recently prepared sample of tetramethylthiophene with Pyrex-filtered u.v. light gave rise to a spectrum with a(3 H) 2.5, a(4 H) 13.5, a(1 H) 21.4 G, g 2.0080. Three months later a solution in trifluoroacetic acid, with or without mercury(II) trifluoroacetate, gave rise to the same spectrum as observed in sulphuric acid, a(6 H) 16.16, a(6 H) 3.44 G.

Conclusions.—The proton hyperfine coupling constants at corresponding positions are very similar in the radical cations of pyrroles, furans, or thiophenes. The ψ_S MO (**4**) with a high electron density at the electronegative heteroatom is lower in energy than the ψ_A MO (**3**) with a node through the heteroatom. In all three species the SOMO is therefore ψ_A with the coefficients X 0.000, C(2),(5) 0.601, C(3),(4) 0.372.

A similar electronic configuration is approached by cyclopentadienyl radicals carrying a strongly electron-attracting substituent; for example, the $Cl_3SiC_5H_4^{\bullet}$ radical shows a(H-2,5) 11.5, a(H-3,4) 3.8 G at 173 K,[14] to be compared with the values of a(Me-2,5) *ca.* 16, and a(H-3,4) *ca.* 3.5 G in pyrrole, furan, and thiophene radical cations.

The same coefficients apply to the SOMO of the cyclopentadiene radical cations with four rather than five π centres,[4–6] and again similar hyperfine couplings constants are observed, *e.g.* $Me_4C_5H_2^{+\bullet}$, a(2 Me) 15.2, a(2 Me) 4.0 G.[6]

At low levels of doping, the charged defects in polymers with

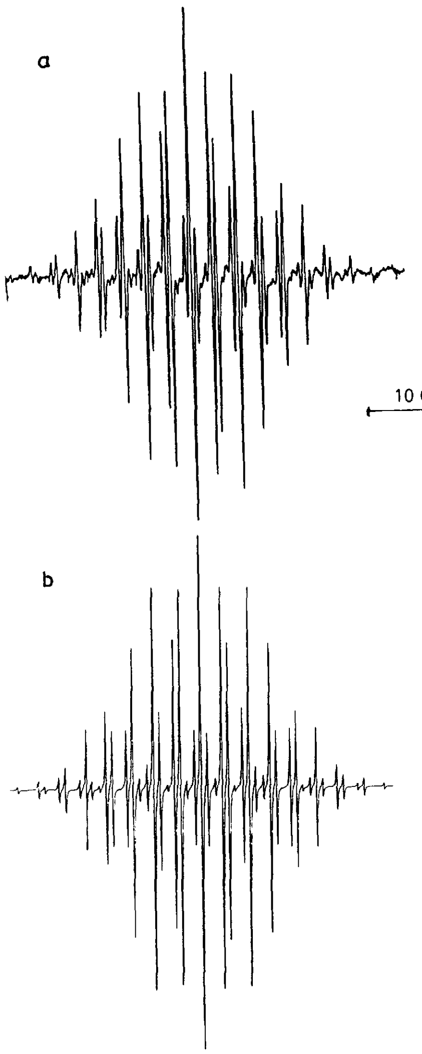

Figure 5. (a) E.s.r. spectrum obtained by photolysis of a solution of 2,5-dimethylthiophene in trifluoroacetic acid at -9 °C. (b) Computer simulation, with a(6 H) 4.9, a(6 H) 2.1 G

high conductivity (*e.g.* polyacetylene, polypyrrole, or polythiophene) are due to radical cations (polarons)[15] and our observations of the spectra of closely related radical cations provide models for these systems. The nature of the paramagnetic solids which we obtained from the oxidation of pyrrole and of thiophene is being further examined.

Experimental

The preparation of novel compounds, new routes to known compounds, and new data on known compounds were as follows.

Octane-3,6-dione.—This was prepared by an extension of Stetter and Kuhlmann's method for the addition of aldehydes to methyl vinyl ketone.[16] A mixture of propanal (3.41 g, 58.7 mmol), pent-1-en-3-one (4.93 g, 58.6 mmol), triethylamine (2.48 g), 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride[17] (2.58 g), and ethanol (25 cm^3) was stirred under reflux under nitrogen for 21 h. The solvent was removed and the residue was taken up in ether and decolorised with active carbon, yielding octane-3,6-dione (4.81 g, 58%), b.p. 110—115 °C at 12 mmHg (Found: C, 67.2; H, 9.6. Calc. for $C_8H_{14}O_2$: C, 67.5; H, 9.9%), δ_H($CDCl_3$) 1.05 (t, 6 H, CH_3, J 7 Hz), 2.49 (q, 4 H, CH_2Me), and 2.69 (s, 4 H, CH_2CH_2).

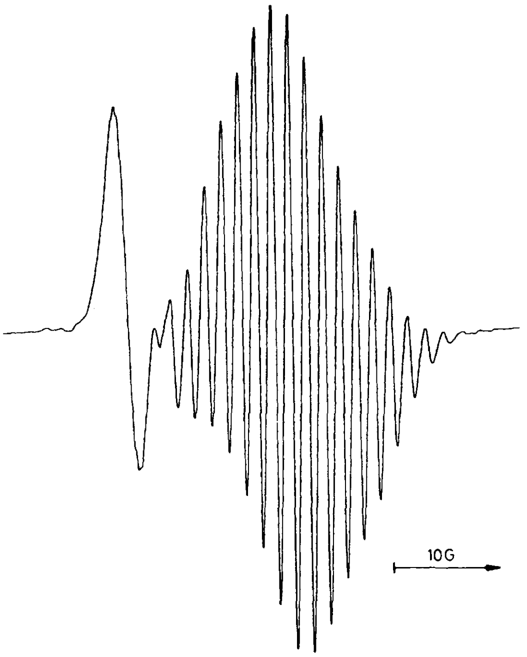

Figure 6. E.s.r. spectrum obtain by photolysis of a solution of 2,5-di-t-butylthiophene in trifluoroacetic acid containing thallium trifluoroacetate at -11 °C

1-Propyl-2,5-diethylpyrrole.—The pyrroles were prepared by the Texier-Boullet method of condensing an amine and a 1,4-dione in the presence of montmorrillonite clay as a catalyst.[18] Details of one such preparation are given; the other pyrroles which follow were prepared by a similar method. Octane-3,6-dione (0.5 g, 3.52 mmol) was dispersed on montmorrillonite K10 (Fluka; 2.5 g) by thorough mixing. To this, propylamine (0.215 g, 3.64 mmol) was added dropwise with stirring and intermittent cooling. After 24 h at room temperature, the product was extracted into dichloromethane, and quickly filtered through silica and dried to give *1-propyl-2,5-diethylpyrrole* (0.523 g, 90%), b.p. 100 °C at 1.0 mmHg (Found: C, 79.9; H, 11.3; N, 8.5. $C_{11}H_{19}N$ requires C, 79.9; H, 11.6; N, 8.5%), δ_{EH}($CDCl_3$) 0.80—1.96 (m, 11 H), 2.56 (q, 4 H, CH_2Me), 3.56—3.80 (m, 2 H, NCH_2), and 5.80 (s, 2 H, =CH-).

1-Butyl-2,5-diethylpyrrole.—Octane-3,6-dione (0.285 g), montmorrillonite (2.5 g), and butylamine (0.150 g) gave the *pyrrole* (0.340 g, 95%), b.p. 100 °C at 0.6 mmHg (Found: C, 79.9; H, 11.6; N, 7.9. $C_{12}H_{21}N$ requires C, 80.4; H, 11.8; N, 7.8%), δ_H($CDCl_3$) 0.86—2.0 (m, 13 H), 2.56 (q, 4 H, CH_2Me), 3.46—3.86 (m, 2 H, NCH_2), and 5.78 (s, 2 H, =CH-).

1-Isopropyl-2,5-diethylpyrrole.—Under the same conditions, isopropylamine showed little reaction after 25 h at room temperature. A mixture of octane-3,6-dione (0.285 g, 2.01 mmol), montmorrillonite (*ca.* 3.0 g), and isopropylamine (*ca.* 1.8 g, 30 mmol) was kept at room temperature for 6 days yielding the pyrrole (0.20 g) containing some dione, δ_H($CDCl_3$) 1.23 (t, 6 H, *Me*CH_2), 1.44 (d, 6 H, *Me*$_2$CH, J 7 Hz), 2.62 (q, 4 H, MeCH_2, J 7 Hz), 4.4 (septet, 1 H, NCH), and 5.76 (s, 2 H, =CH-).

1-Isopropyl-2,5-dimethylpyrrole.—A mixture of hexane-2,5-dione (0.50 g), montmorrillonite (2.0 g), and isopropylamine (2.0 g) was kept at room temperature for 8 days. The crude product in dichloromethane was filtered through silica and dried giving the *pyrrole* (0.60 g, 99%) which was purified by distillation, b.p. 100.5 °C at 12 mmHg (Found: C, 78.3; H, 11.4; N, 10.4. $C_9H_{15}N$ requires C, 78.8; H, 11.0; N, 10.2%), δ_H($CDCl_3$)

1.44 (d, 6 H, CHMe_2, *J* 7 Hz), 2.28 (s, 6 H, CH_3), 4.38 (septet, 1 H, CHMe$_2$), and 5.68 (s, 2 H, =CH–).

Ethylenebis-(2,5-*diethylpyrrole*).—A mixture of octane-3,6-dione (0.568 g), montmorrillonite (3.0 g), and ethylenediamine (0.120 g) was kept at room temperature for 5 days. The crude *product* (0.51 g, 94%) was purified by recrystallisation from ethanol, m.p. 78 °C (Found: C, 78.9; H, 10.2; N, 10.4. $C_{18}H_{28}N_2$ requires C, 79.4; H, 10.4; N, 10.3%), $\delta_H(CDCl_3)$ 1.22 (t, 12 H, CH$_2\mathit{Me}$, *J* 7 Hz), 2.34 (q, 8 H, CH_2Me *J* 7 Hz), 3.72 (s, 4 H, NCH_2), and 5.60 (s, 4 H, -CH=).

Ethylenebis-(2,5-*dimethylpyrrole*).—This had $\delta_H(CHCl_3)$ 1.98 (s, 12 H, Me), 3.88 (s, 4 H, NCH_2), and 5.72 (s, 4 H, -CH=).[18]

1-*Phenyl*-2,5-*dimethylpyrrole*.—This had $\delta_H(CHCl_3)$ 2.0 (s, 6 H, Me), 5.88 (s, 2 H, -CH=), and 6.90—7.44 (m, 5 H, Ph).[18]

1-*Benzyl*-2,5-*dimethylpyrrole*.—This had $\delta_H(CHCl_3)$ 2.06 (s, 6 H, Me), 4.86 (s, 2 H, NCH_2), 5.86 (s, 2 H, =CH–), and 6.28—7.28 (m, 5 H, PhO).[18]

Trimethylenebis-(2,5-*dimethylpyrrole*).—A mixture of hexane-2,5-dione (0.600 g), montmorrillonite (2.5 g), and trimethylenediamine (0.195 g) was kept at room temperature for 22 h, yielding the *pyrrole* (0.565 g, 93%), m.p. 81—82 °C (Found: C, 78.0; H, 9.45; N, 12.2. $C_{15}H_{22}N_2$ requires C, 78.2; H, 9.65; N, 12.2%), $\delta_H(CDCl_3)$ 1.7—2.04 (m, 2 H, CCH_2C), 1.94 (s, 12 H, Me), 3.52—3.90 (m, 4 H, NCH_2), and 5.72 (s, 4 H, =CH–).

2,5-*Di-t-butylfuran*.—A solution of tin tetrachloride (13.0 g) in carbon disulphide (15 cm^3) was added to a solution of furan (3.32 g) and t-butyl alcohol (7.1 g) in carbon disulphide (50 cm^3) at 0 °C under nitrogen. The mixture was kept at room temperature overnight, then cooled and treated with dilute hydrochloric acid. From the organic layer, 2,5-*di-t-butylfuran* (1.86 g, 21%) was recovered, b.p. 130 °C at 12 mmHg (Found: C, 79.7; H, 11.4. $C_{12}H_{20}O$ requires C, 79.9; H, 11.2%), δ_H 1.24 (s, 18 H, $\mathrm{Bu^t}$) and 5.34 (s, 2 H, =CH–).

2,5-*Di-t-butylthiophene*.—This had δ_H 1.38 (s, 18 H, $\mathrm{Bu^t}$) and 6.54 (s, 2 H, =CH–).[19]

2,5-*Diethylthiophene*.—A mixture of octane-3,6-dione (0.75 g) 2,4-bis-4-methoxyphenyl-2,4-dithioxo-1,3,2,4-dithiadiphosphetane (Lawesson's reagent; Aldrich; 2.70 g) and toluene was stirred under reflux for 1 h.[20] The cooled mixture was diluted with hexane and filtered through a column of silica gel, giving 2,5-*diethylthiophene* (10.36 g, 49%), b.p. 160 °C (Found: C, 68.8; H, 8.6. $C_8H_{12}S$ requires C, 68.5; H, 8.6%), $\delta_H(CDCl_3)$ 1.31 (t, 6 H, CH_3, *J* 7 Hz), 2.78 (q, 4 H, CH_2), and 6.54 (s, 2 H, =CH–).

2,3,4,5-*Tetramethylthiophene*.[21]—The reaction of 2,5-dimethylthiophene with trioxane in the presence of HCl gave 2,5-dimethyl-3,4-bischloromethylthiophene, $\delta_H(CDCl_3)$ 2.4 (s, 6 H, Me) and 4.58 (s, 4 H, CH_2Cl). Reduction of this with lithium aluminium hydride gave the tetramethylthiophene, $\delta_H(CDCl_3)$ 1.9 (s, 6 H, Me) and 2.2 (s, 6 H, Me), *m/z* 140 (*M*) and 125 ($M - CH_3$).

E.s.r. Spectroscopy.—E.s.r. spectra were recorded using a Varian E4 or E109 spectrometer with the facility for photolysis of samples in the cavity with light from a 500 W high-pressure mercury arc provided with neutral density and glass filters.

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