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SPIN DENSITY DISTRIBUTIONS AND CONFORMATIONAL PROPERTIES OF SOME THIOPHEN RADICALS

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Abstract—The ESR spectra of the 2-thenyl,3-thenyl and 5-methyl-2-thenyl radicals, and of the radical anions of thiophen-2-aldehyde, thiophen-3-aldehyde, 2-acetyl-thiophen and 2,2′-dithienone have been recorded in fluid solutions. The ketyls of thiophen-2-aldehyde and 2-acetylthiophen give overlapping spectra from O-*cis* and O-*trans* isomers present in unequal amounts. The spin distributions in the radicals studied are compared with the results of semi-empirical molecular orbital calculations.

THE nature of the bonding in heterocyclic sulphur compounds and in particular the possible role of *d*-orbitals has long been a subject of interest; two recent articles have dealt with this topic in some detail.[1, 2] ESR studies of sulphur containing radical anions have also been reviewed fairly recently.[3] Electron resonance studies in solution are not likely to provide any direct evidence for the participation of *d*-orbitals in bonding because the isotropic nuclear hyperfine coupling constants depend on *s*-electron spin densities. Spin density in *d*-orbitals only affects the observed splittings by polarizing valence and inner shell electrons. The coupling constants do however provide a useful test of methods employed to calculate semi-empirical wavefunctions for sulphur heterocycles. In particular proton splittings can be related to π-electron spin densities by well established procedures.

Although several investigations have been reported many of these have been concerned with relatively large systems such as thioxanthones or dibenzothiophens.[4] Rather fewer measurements have been performed on radicals derived from thiophen itself. Those described in the literature include the radical anions of nitrothiophens,[5] some thienyl-phenyl ketones,[6] and 2,2′-dithienone, 2,2′-dithenil and 3,3′-dithenil.[7] These systems all contain other heteroatoms apart from sulphur which increases the number of parameters required in semi-empirical calculations. We have already briefly reported the ESR spectra of 2-thenyl and 3-thenyl which are analogues of the benzyl radical.[8] Some thienyl-phenyl and trithenylmethyl radicals have also been observed recently.[9] We now present further details of our work on thenyl radicals and some new data on ketyl radicals derived from the thiophen aldehydes and 2-acetylthiophen.

RESULTS

Well resolved spectra were obtained from all of the thenyl radicals. The assignment of coupling constants in Table 1 has been made on the basis of MO calculations to be discussed later and is subject to some uncertainty. The results for the 5-methyl-2-thenyl radical lend support to our previous assignment of the larger of the 8·26 and 7·89 G doublets in the 2-thenyl spectrum to the 3-position. The pattern of hyperfine

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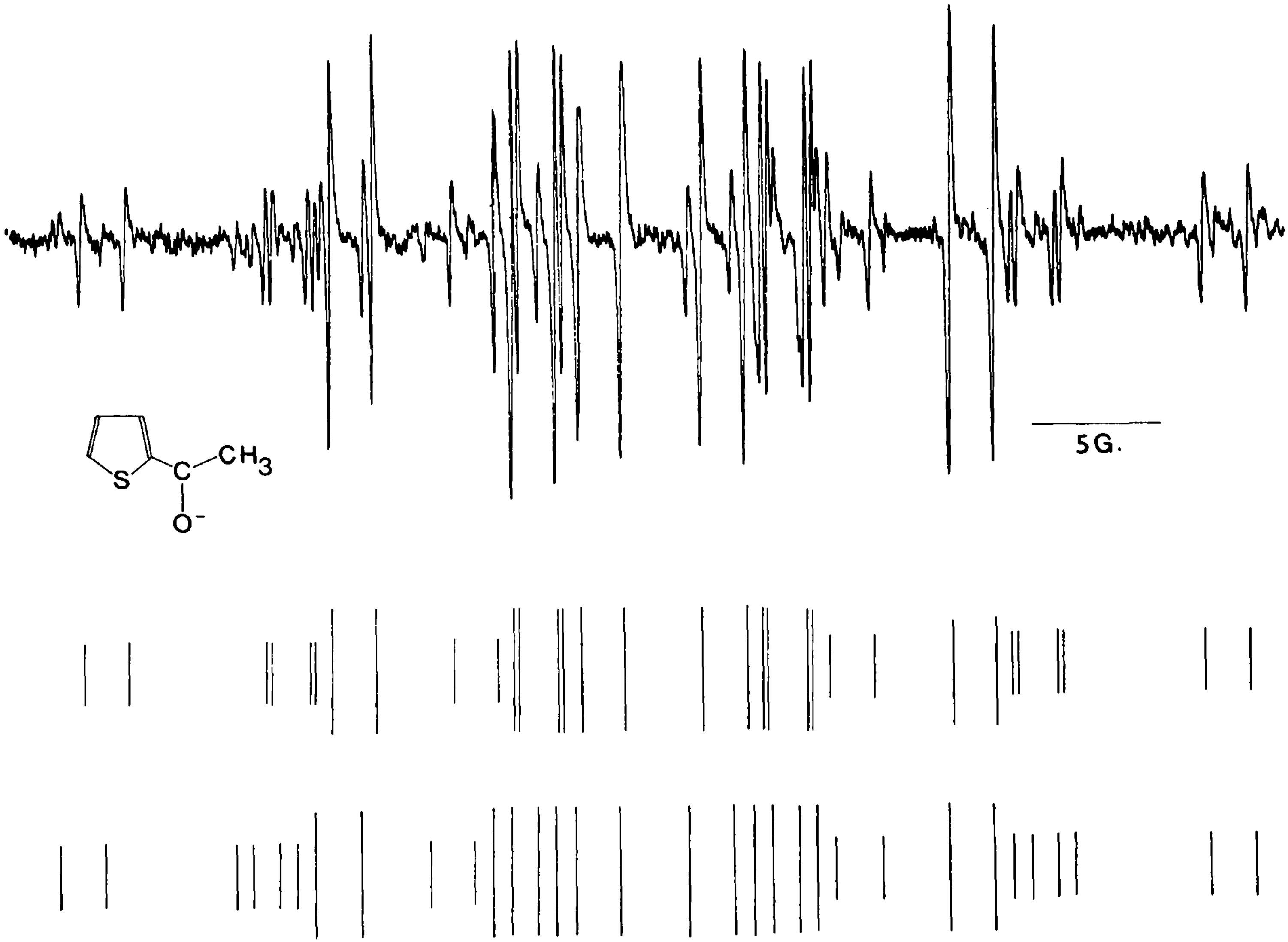

Fig. The ESR spectrum obtained from the 2-acetyl-thiophene radical anion with stick reconstructions of the lines attributed to the O-*cis* and O-*trans* isomers.

splittings is similar to that found in the nitrothiophen radical anions which were also assigned by comparison with methyl substituted compounds.[5] The assignment of the two small doublets in the 3-thenyl spectrum is essentially arbitrary. A discussion of the inequivalence of methylene protons in the thenyl radicals and related systems in terms of σ-π configuration interaction has been presented elsewhere.[10]

The ESR results obtained from the 2-acetyl-thiophen ketyl are shown in Fig 1. The trace consists of two overlapping spectra present in unequal amounts which we believe arise from the O-*cis* and O-*trans* isomers, I and II, respectively. Similar results were obtained from thiophen-2-aldehyde. The relative strengths of the overlapping spectra are temperature dependent as expected for two species in thermal equilibrium. Only one isomer was reported in an earlier investigation[6] of the 2-acetylthiophen ketyl in which the radical was obtained by electrolytic reduction in DME or DMF. This may simply be due to the fact that lower resolution is often obtained in aprotic solvents compared with methanol.

I II

TABLE 1. HYPERFINE COUPLING CONSTANTS OF SOME THIOPHEN RADICALS

Radical	$\|a_2\|$	$\|a_3\|$	$\|a_4\|$	$\|a_5\|$	
2-Thenyl	—	8·26[a]	1·62	7·89[a]	a_{CH_2} = 14·22, 13·97
3-Thenyl	8·94	—	0·74[a]	1·86[a]	a_{CH_2} = 16·39, 16·89
5-Methyl-2-thenyl	—	8·52	1·36	8·28[b]	a_{CH_2} = 13·56, 13·23
Ketyl radicals					
Thiophen-2-aldehyde I[c]	—	7·29[a]	1·73	7·42[a]	a_{CHO} = 11·24
II	—	6·43[a]	1·67	7·29[a]	a_{CHO} = 11·87
2-Acetyl-thiophen I	—	7·16[a]	1·73	7·40[a]	a_{CH_3} = 9·75
II	—	6·91[a]	1·73	7·65[a]	a_{CH_3} = 10·12
Thiophen-3-aldehyde	8·57	—	0·62[a]	1·24[a]	a_{CHO} = 13·50
2,2′-dithienone	—	4·87[a]	1·09	4·15[a]	

[a] Assignment could be reversed.

[b] Quartet from three equivalent protons.

[c] I is the most abundant isomer in each case.

The signals from the thiophen-3-aldehyde ketyl were rather weak and poorly resolved and as a result we have only been able to observe a single isomer. The lower stability of this radical compared with those from 2-substituted thiophens is in accord with the increased localization of the unpaired electron on the substituent.

A spectrum attributed to the 2,2′-dithienone radical anion has been observed by Strom *et al.*[7] during the air oxidation of 2,2′-dithienyl methane in a 4 : 1 mixture of DMSO and t-butanol containing potassium t-butoxide. Their triplet splittings of 4·1, 3·7 and 0·9 G are smaller than our values as expected on going to an aprotic solvent. The coupling constants obtained by Kaper *et al.*[6] for the 2-acetyl-thiophen ketyl in DMF are also lower than our results in methanol. Photolysis of 2,2′-dithienone in basic methanol produces an intense ESR spectrum. Only a single species was observed in our experiments at room temp which suggests that rotation of the thienyl rings is rapid. The rotation of the phenyl rings in the benzophenone ketyl is also rapid at ambient temperatures but it has recently been found that at −100° and below the *ortho* and *meta* protons become inequivalent[11] as in the ketyls of benzaldehyde and acetophenone.[12] Like benzophenone 2,2′-dithienone is readily reduced by alkali metals in ether solvents. The spectra then exhibit additional splittings from the metal nucleus because of ion-pairing.

Molecular orbital calculations

To assist in the interpretation of the experimental coupling constants, MO calculations were carried out using McLachlan's method.[13] We have used both *p*- and *d*-models for the S atom, the necessary parameters being taken from the work of Lucken.[4, 5] In the *p*-model $\alpha_S = \alpha + \beta$ and $\beta_{CS} = 0{\cdot}7\beta$; in the *d*-model $\alpha_S = \alpha$, $\beta_{CS} = 0{\cdot}8\beta$, and $\beta_{SS'} = \beta$. For the carbonyl groups we took $\alpha_O = \alpha + 2{\cdot}2\beta$, $\beta_{CO} = 1{\cdot}6\beta$ and an auxiliary inductive parameter of $0{\cdot}1\beta$ at the C atom. Some of the coupling constants calculated from the theoretical spin densities and McConnell's relationship with $Q = -22{\cdot}5$ G are given in Table 2.

TABLE 2. HYPERFINE SPLITTINGS CALCULATED USING MOLECULAR ORBITAL THEORY

Radical	Model	a_2	a_3	a_4	a_5	$a_{CH_2, CHO}$
2-Thenyl	p	—	−6·91	+2·29	−5·32	−15·51
	d	—	−5·14	+2·06	−4·58	−16.49
3-Thenyl	p	−7·75	—	−1·00	+1·40	−19·01
	d	−5·68	—	−2·35	+1·74	−18·06
Thiophen-2-aldehyde	p	—	−6·24	+2·04	−6·44	−8·72
	d	—	−4·95	+1·48	−6·52	−8·17
Thiophen-3-aldehyde	p	−10·86	—	−0·51	+1·37	−11·04
	d	−6·66	—	−1·71	+0·89	−9·32

DISCUSSION

Both MO models give coupling constants in reasonable agreement with experiment, the *p*-model being slightly superior. The assignment of the two small doublet splittings in the 3-thenyl and thiophen-3-aldehyde radicals is dependent upon the model used. The *p*-method gives $a_5 > a_4$ whereas the *d*-model gives the reverse. An experimental assignment of a_4 and a_5 would facilitate a choice between the two models but as the small splittings are particularly sensitive to the parameters used for the S atom, it is doubtful if such a determination would be of any great significance. We have not made any allowance for the asymmetry in spin distribution introduced by restricted rotation of the ketyl groups because of the extra parameters this would involve.

As was noted earlier the assignment of a_3 and a_5 in 2-thenyl is supported by the results from 5-methyl-2-thenyl, but the situation in the other 2-substituted thiophens is open to speculation. Strom *et al.*[7] attribute the largest triplet in 2,2′-dithienone to the 5,5′-protons whereas our calculations favour the 3,3′-protons although the assignment is quite sensitive to the parameters chosen for the O atom.* By analogy with the benzophenone and benzaldehyde ketyls and the benzyl radical one would expect

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* Recent work[22] on the 5,5′-dideutero-2,2′-dithienone ketyl has confirmed that $a_3 > a_5$.

$a_5 > a_3$. In view of the difficulties found[14] in accounting for the relative magnitude of the *ortho* and *para* proton splittings in benzyl it is unwise to place too much reliance on the molecular orbital calculations in the present instance. In the case of the benzyl radical it seems probable that the difficulties can be overcome[15] by taking into account bond length variations in the benzene ring. Such effects might well be even more important in the thiophene ring.

As we have already indicated the overlapping spectra observed in the experiments with thiophen-2-aldehyde and 2-acetyl-thiophen almost certainly arise from the presence of O-*cis* and O-*trans* isomers in thermal equilibrium. Hindered rotation in the related molecule, furan-2-aldehyde, has been investigated by a variety of methods including NMR[16] and vapour-phase, far IR spectroscopy.[17] The kinetics and thermodynamics of internal rotation in both furan and thiophen-2-aldehydes has recently been investigated using ultrasonic pulse techniques.[18] The spectroscopic studies have established that in furan-2-aldehyde the O-*trans* isomer is the more stable; at 216°K in solution[16] $\Delta G = 2{\cdot}43$, $\Delta H = 4{\cdot}39$ kJ.mol^{-1} and $\Delta S = 9{\cdot}08$ JK^{-1}. The ultrasonic relaxation experiments gave $\Delta H \leqslant 6{\cdot}3$ for the furan and $\Delta H \leqslant 6{\cdot}7$ kJ.mol^{-1} for the thiophen. In the absence of spectroscopic information it was assumed that the O-*trans* isomer of thiophen-2-aldehyde was also the more stable. From measurements of relative line intensities as a function of temperature we find $\Delta H = 2{\cdot}9 \pm 0{\cdot}4$ for the radical anion of 2-acetyl-thiophen and $\Delta H = 4{\cdot}2 \pm 0{\cdot}4$ kJ.mol^{-1} for the thiophen-2-aldehyde ketyl. These results are of the right order of magnitude and the lower value for the acetyl compound seems reasonable in view of the greater size of the methyl group compared with the aldehyde proton.

Finally by considering differences in the coupling constants of the two overlapping spectra we can attempt to decide which is the more stable isomer. In the benzaldehyde radical anion[12] the largest *ortho* proton splitting is associated with the position *trans* to the oxygen atom. We might therefore expect that in the 2-substituted thiophen radicals I will have a larger value of a_3 than II. We would also expect I to have a smaller spin density on sulphur and hence a lower g-factor. In both the aldehyde and ketyl radicals the spectrum of the least abundant radical is centred to low field of the major species and hence has a higher g-factor. We therefore tentatively suggest that the O-*cis* radical is the thermodynamically most stable form in each case, thus reversing the situation found in the neutral molecules. Since the radicals are charged species and have been studied in strongly solvating media a more detailed comparison is of doubtful validity.

EXPERIMENTAL

All the radicals were generated by photolysis of solutions within the cavity of a Varian E3 spectrometer using techniques previously described.[10, 19] The thenyl radicals were produced by the reaction of t-butoxy radicals with a methyl thiophene; the aldehydes and ketones were photolyzed in 10^{-2}M solns of NaOMe in MeOH. Sample temps were recorded with a Comark 1605 electronic thermometer by immersing a Cr/Al thermocouple into the sample before and after recording the spectrum.

Thiophene-2-aldehyde and 2-acetyl-thiophene were obtained from Koch-Light Limited and 2- and 3-methylthiophene from Ralph Emanuel Limited. A sample of 2,5-dimethylthiophene was kindly donated by Dr. B. G. Odell of Cambridge University. Thiophene-3-aldehyde was prepared as described by Campaigne *et al.*,[20] 2,2'-dithienone was prepared from thiophene-2-carboxylic acid.[21]

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