

Temperature-dependent Hyperfine Splitting Constants in the Electron Spin Resonance Spectra of Some Thienylmethanone Radical Anions

Christopher J. Leach and Brian J. Tabner*

The Department of Chemistry, The University of Lancaster, Lancaster LA1 4YA

The radical anions of di-2-thienyl- and phenyl-2-thienyl-methanone have been prepared by electrochemical reduction in dimethylformamide, dimethyl sulphoxide, and acetonitrile. The e.s.r. spectrum of the former has been interpreted in terms of the presence of both the *trans,trans*- and *cis,trans*-conformers, and the activation parameters for the interconversion between these conformers have been determined. The temperature dependence of the hyperfine splitting constants in each conformer has also been determined, and in dimethylformamide reveals a temperature-independent region between 263 and 293 K. The individual conformers were not observed for the phenyl-2-thienylmethanone radical anion.

We have previously reported the temperature dependence of the hyperfine splitting constants in some heterocyclic ethanedione radical anions.¹ In each of these radical anions there are a number of possible rotational conformers, and one explanation of the observed temperature dependence could be that the position of the equilibrium between these conformers varies with temperature. In order to investigate this possibility further, it seemed worthwhile to extend this study to include the corresponding methanone radical anions. Some of these radical anions have been studied previously, when formed by photolysis or by alkali metal reduction.² Under these conditions it was possible, particularly at low temperature, to observe an e.s.r. spectrum consistent with the presence of two conformational isomers.

In order to compare our results with those for the ethanedione radical anions, an extensive study of the radical anions formed by electrochemical reduction in the same solvents (dimethylformamide, acetonitrile, and dimethyl sulphoxide) is required. If the e.s.r. spectrum of the radical anions in these solvents can also be interpreted in terms of more than one conformer it should be possible to investigate the temperature dependence of the hyperfine splitting constants of the individual conformers. The magnitude of da/dT for each conformer should enable typical values to be determined in the absence of any possible equilibrium contribution.

Experimental

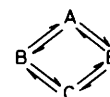
Materials.—Dimethylformamide and dimethyl sulphoxide (both Aldrich) were distilled under reduced pressure before use; acetonitrile (B.D.H.) was used as supplied. All three solvents were stored over a 4 Å molecular sieve.

Di-2-thienylmethanone was prepared by direct acylation of thiophene with 2-thenoic acid,³ and was purified by recrystallisation from aqueous ethanol (m.p. 87–88 °C). Phenyl-2-thienylmethanone was prepared by reaction of lithium benzoate with 2-thienyl-lithium.⁴ The product was recrystallised from light petroleum (b.p. 60–80 °C) to give the pure methanone (m.p. 46–47 °C).

Procedure.—The concentrations of the solutions of the parent ketones, for electrochemical reduction, were in the range $1\text{--}4 \times 10^{-3}$ mol dm⁻³, with tetra-*n*-butylammonium iodide (B.D.H.) as supporting electrolyte (0.1–0.2 mol dm⁻³). Solutions of the radical anions were prepared for e.s.r. study as described previously.⁵

Spectroscopic Measurements.—E.s.r. spectra were recorded

with a Varian E3 spectrometer. The magnetic field sweep was calibrated using Fremy's salt⁶ and the temperature of the samples was controlled by means of a Varian E 4557 variable-temperature unit. Computer simulations of e.s.r. spectra were obtained using a Data General Nova 1220 computer on line to the spectrometer or with an ICL 1905E computer linked to a Calcomp plotter. The program required for the simulation of the e.s.r. spectra of these radical anions is that appropriate to a four-jump model, to allow for the two possible symmetric conformers (A and C) and the unsymmetric conformer (B) (Scheme 1). However, as explained later, the spectrum of only



Scheme 1.

one of the two possible symmetric conformers was observed and the program employed is based on the modified Bloch equations for a 'blocked' three-jump model (Scheme 2). The



Scheme 2.

hyperfine splitting constants quoted from these simulations are considered accurate to within ± 1 μ T. The temperature coefficients, da/dT , for the variation in the hyperfine splitting constants with temperature were obtained by a least-squares analysis and are considered accurate to within $\pm 1 \times 10^{-2}$ μ T K⁻¹. (The absolute magnitude of a was used to calculate the values of da/dT quoted in this paper.)

Results and Discussion

Di-2-thienylmethanone.—This ketone was reduced electrochemically in all three solvents to give a green solution of the radical anion; slightly greater voltages and ketone concentrations were required in dimethyl sulphoxide and in acetonitrile than in dimethylformamide. We describe first the e.s.r. spectra obtained in dimethylformamide. Spectra were recorded over the temperature range 223–353 K. At the high end of the range the spectra were slightly asymmetric, this feature becoming more pronounced at the low end. The spectrum obtained at 223 K

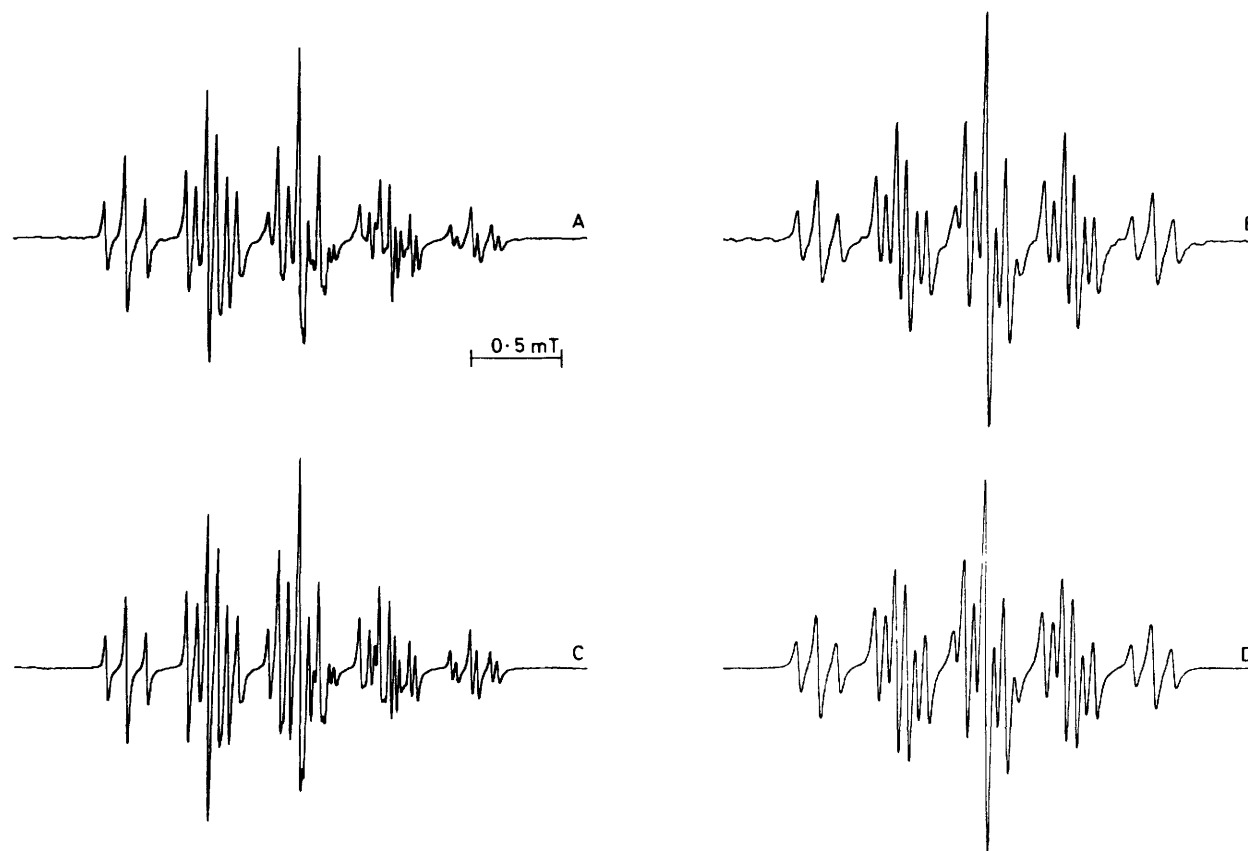
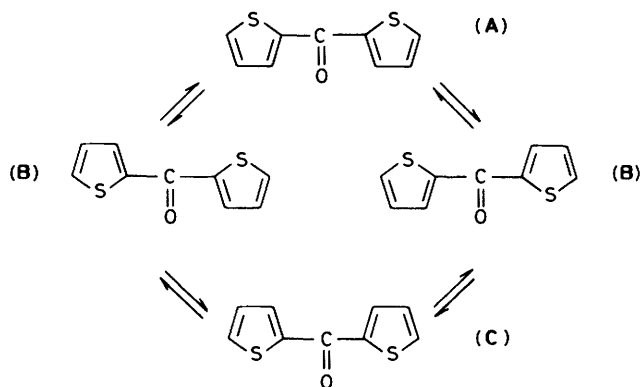


Figure 1. The experimental e.s.r. spectra of the di-2-thienylmethanone radical anion, in dimethylformamide, at 223 K (A) and 333 K (B) together with their computer simulations [(C) and (D) respectively; parameters as given in Table 1]

[Figure 1(a)] clearly indicates the presence of two species. This situation is similar to that reported by Guerra *et al.* for this radical anion when prepared photolytically or by alkali metal reduction.² It appears therefore that when the radical anion is produced by electrochemical reduction in dimethylformamide it exists as two interconverting conformers. Since there is no evidence in the e.s.r. spectrum for the third conformer we have attempted to computer-simulate the spectrum at 223 K in terms of one symmetric (either the *trans,trans*- or the *cis,cis*-; see Scheme 3) conformer [(A) or (C)] and of the asymmetric (*cis,trans*-) conformer (B).



Scheme 3.

The e.s.r. spectrum in Figure 1(a) can be interpreted in terms of two species. One of these, with $a(2H)$ 423, 375, and 93 μT , is the symmetric isomer [either (A) or (C)] and the other, with $a(H)$ 441 and 430, and $a(2H)$ 379 and 95 μT (and a lower g -value) is the asymmetric conformer (B). The difference in the hyperfine splitting constants for the same ring position in the two conformers is a result of the electrostatic interaction between the carbonyl oxygen and the thiophene ring, leading to a greater spin density (and a lower g -value) on the ring atom *trans* with respect to the carbonyl group.² The symmetric conformer has a higher g -value than the *cis,trans*-conformer (B), suggesting, therefore, that this is the *trans,trans*-conformer. This conclusion is supported by the higher 3,3'-H splitting constant observed in the *cis,trans*-conformer as compared with that in the symmetric conformer. We therefore conclude that the symmetric conformer observed is the *trans,trans*-isomer (A).

A complete computer simulation of each spectrum was attempted, employing the modified Bloch equations appropriate to a 'blocked' three-jump model. The results of two of these simulations are illustrated in Figure 1(c) and (d) at 223 and 333 K, respectively, and the values of the best-fit hyperfine splitting constants for each isomer at each temperature and the values of $\tau_{trans,trans}$ and $\tau_{cis,trans}$ are summarised in Table 1. Clearly the hyperfine splitting constants for each conformer are temperature-dependent. It is reasonable, therefore, to suggest that this would also be the case for the corresponding conformers in the ethanedione radical anions previously reported,¹ and that in the latter case the values of da/dT observed do not result from a shift in equilibrium position although this could be an additional contribution.

Table 1. Hyperfine splitting constants (in μT) for the di-2-thienylmethanone radical anion in dimethylformamide, acetonitrile, and dimethyl sulphoxide, obtained by best-fit computer simulation, together with the appropriate values of $\tau_{trans,trans}$ (τ_{tt}) and $\tau_{cis,trans}$ (τ_{ct}) (in s)

T/K	<i>trans,trans</i> -Conformer				<i>cis,trans</i> -Conformer				
	$\alpha(3,3\text{'-H})$	$\alpha(4,4\text{'-H})$	$\alpha(5,5\text{'-H})$	τ_{tt}	$\alpha(3\text{-H})$	$\alpha(3\text{'-H})$	$\alpha(4,4\text{'-H})$	$\alpha(5,5\text{'-H})$	τ_{ct}
Dimethylformamide									
223	423	(-) 93	375		441	430	(-) 95	379	
233	422.5	(-) 93	374.5		441	429	(-) 95	378.5	
243	421	(-) 93	373	10	439	428	(-) 95	377	3.75
253	421	(-) 93	373	5.5	439	429	(-) 95	377	2.5
263	418	(-) 93	372	3.4	436	425	(-) 95	376	1.5
273	418	(-) 93	372	2.1	436	425	(-) 95	376	0.9
283	418	(-) 93	372	1.0	436	425	(-) 95	376	0.4
293	418	(-) 93	372	0.7	436	425	(-) 95	376	0.3
313	414	(-) 92	368	0.45	432	421	(-) 94	372	0.2
333	410	(-) 92	364	0.225	428	417	(-) 94	368	0.1
353	408	(-) 92	363	0.155	426	415	(-) 94	367	0.07
Acetonitrile									
253	429	(-) 93	381	2.1	447	436	(-) 95	385	0.9
263	427	(-) 93	379	1.0	444	433	(-) 95	383	0.4
273	425	(-) 93	377	0.7	442	431	(-) 95	381	0.3
283	422	(-) 92	375	0.5	439	428	(-) 94	379	0.2
303	419	(-) 92	372	0.3	437	426	(-) 94	377	0.13
313	418	(-) 92	371	0.2	436	425	(-) 94	376	0.1
333	417	(-) 93	369	0.155	435	424	(-) 95	373	0.07
Dimethyl sulphoxide									
293	419	(-) 93	372	0.45	437	426	(-) 95	376	0.2
313	416	(-) 93	369	0.225	434	423	(-) 95	372	0.1
333	413	(-) 93	366	0.125	431	420	(-) 95	370	0.05
353	411	(-) 93	364	0.07	429	418	(-) 95	368	0.03

Another feature of these results is that the variation of each splitting constant with temperature does not follow a straightforward trend, but reveals a region between 263 and 293 K in which the splitting constants are virtually independent of temperature (see Figure 2). In the three solvents we have employed this feature seems to be unique to dimethylformamide. A similar feature has been observed by Branca *et al.* for the 3-nitrobenzaldehyde radical anion prepared by reduction with CH_3ONa in dimethylformamide.⁷ The hyperfine splitting constants of this latter radical anion were also virtually independent of temperature over part of the temperature range, varying linearly with temperature both above and below the feature. In this latter system the feature was interpreted in terms of a rapid equilibration between ion pairs and free ions. However, in our system the only possible counterion present is Bu^n_4N^+ , which is less likely to form ion pairs than Na^+ . Since the feature is not observed for the di-2-thienylmethanone radical anion in dimethyl sulphoxide and acetonitrile it is possible that it is due to a change in the nature of the solvation of the radical anion.

Spectra of the radical anion were also recorded and computer-simulated over a temperature range in both acetonitrile and dimethyl sulphoxide. In acetonitrile the spectra at the low end of the temperature range were again interpreted in terms of the *trans,trans*- and *cis,trans*-conformers, and the same procedure was followed as already described to obtain the parameters for these solvents reported in Table 1. As can be seen from the Table the variation of the various hyperfine splitting constants with temperature is linear over the whole of the range, with no apparent temperature-independent region. In dimethyl sulphoxide the lowest temperature at which spectra could be recorded was 293 K and at this temperature the parameters for the individual conformers were not obtainable (*i.e.* the system was already in the 'fast-exchange' region). In order to obtain the

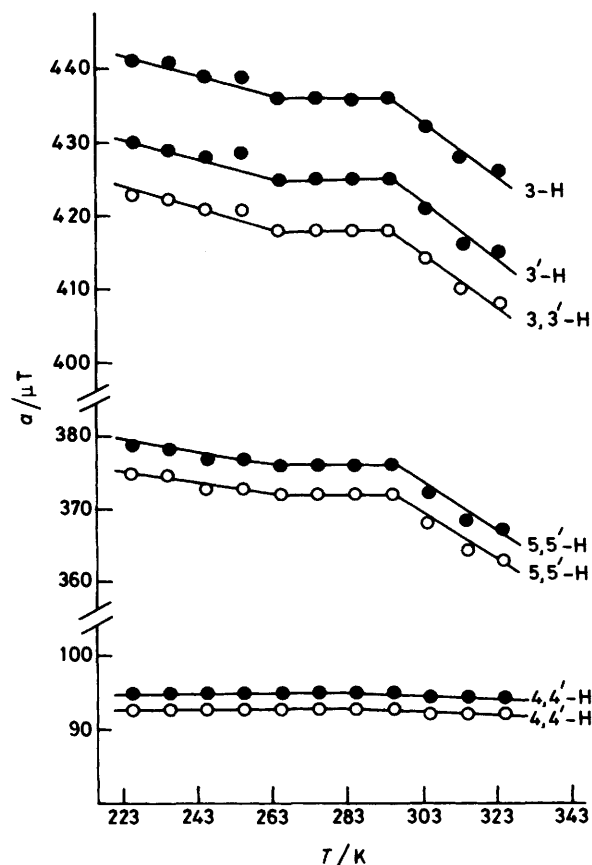
parameters quoted in this solvent the hyperfine splitting constants were assumed to have the same relative proportions as observed in dimethylformamide and acetonitrile. The values quoted in this solvent are therefore merely those used for the purpose of the computer simulation and cannot be verified experimentally for either of the conformers. Consequently although the values of τ quoted for the radical anion in dimethyl sulphoxide are probably correct relative to one another, their absolute values cannot be determined. A comparison of the τ values obtained in dimethylformamide with those obtained in acetonitrile shows that, at the same temperature, the τ value is always smaller in acetonitrile than in dimethylformamide. The interconversion between the isomers is therefore more rapid in acetonitrile than in dimethylformamide.

The values of da/dT obtained for the di-2-thienylmethanone radical anion in dimethylformamide and acetonitrile are summarised in Table 2. It can be seen that the values for a particular proton in the two conformers in the same solvent are very similar to one another and that the values at higher temperatures (293–323 K) in dimethylformamide are very similar to those obtained in acetonitrile.

The complete computer simulation of each experimental spectrum requires, in addition to the splitting constants, values for the lifetimes (τ) of the two conformers; the best-fit values obtained are quoted in Table 1. As can be seen the *trans,trans*-isomer has the greater lifetime in both dimethylformamide and acetonitrile. This could be a result of a reduced repulsion between the S atom and the carbonyl oxygen, but solvation of the carbonyl group could also be an important factor. In all cases a good linear Arrhenius plot ($\ln k$ vs. $1/T$) was obtained and the activation energies for the interconversion between the conformers in both solvents are summarised in Table 3. In both cases the activation energy for the interconversion is slightly greater for the *trans,trans*-conformer, but the difference is

Table 2. Values of da/dT ($\times 10^2/\mu\text{T K}^{-1}$) for each conformer of the di-2-thienylmethanone radical anion in dimethylformamide and acetonitrile

	<i>trans,trans</i> -Conformer			<i>cis,trans</i> -Conformer			
	$da(3,3'\text{-H})/dT$	$da(4,4'\text{-H})/dT$	$da(5,5'\text{-H})/dT$	$da(3\text{-H})/dT$	$da(3'\text{-H})/dT$	$da(4,4'\text{-H})/dT$	$da(5,5'\text{-H})/dT$
HCONMe ₂ ^a	-10.5	-0.9	-6.4	-11.4	-10.3	-0.9	-6.5
HCONMe ₂ ^b	-15.7	-0.9	-14.6	-15.7	-15.7	-0.9	-14.6
MeCN	-15.8	-0.6	-15.2	-14.9	-14.1	-0.6	-14.4

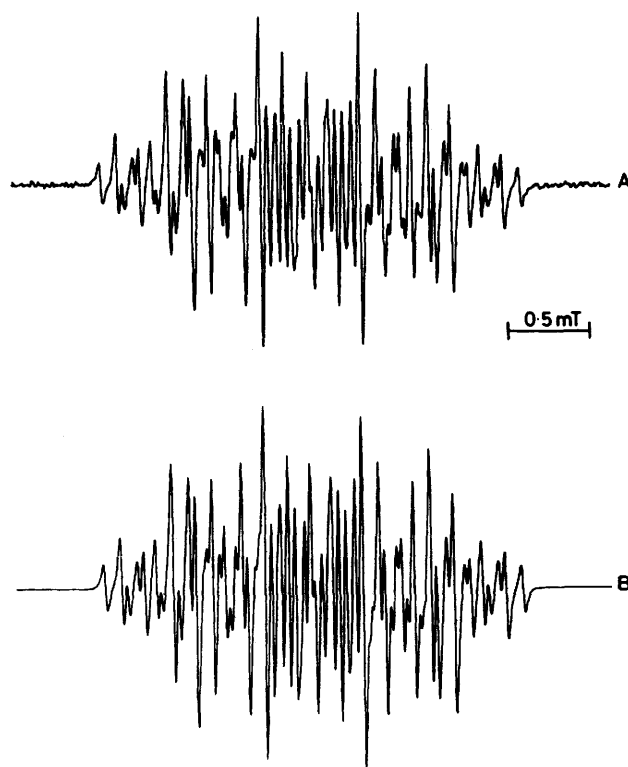
^a 223–263 K. ^b 293–353 K.**Figure 2.** The temperature dependence of the hyperfine splitting constants for the *trans,trans*- (○) and *cis,trans*- (●) conformers of the di-2-thienylmethanone radical anion in dimethylformamide

almost within experimental error. Table 3 also summarises the various values of ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger . One feature of these results is the large negative entropy term. This indicates a rather restricted transition state, consistent with a fairly specific arrangement of solvent molecules presumably in the vicinity of the polar solvation sites.

Phenyl-2-thienylmethanone.—As with the di-2-thienylmethanone radical anion the e.s.r. spectrum of the phenyl-2-thienylmethanone radical anion, prepared by electrochemical reduction, was studied over a wide temperature range in both dimethylformamide and acetonitrile. Unfortunately, however, the spectra showed no evidence for the existence of two (or more) conformers in either solvent. Although conformers of this radical anion would be expected to exist it could be that the spectra are in the 'fast-exchange' region over the temperature range studied. A typical spectrum of the phenyl-2-thienyl-

Table 3. Activation parameters for interconversion from each conformer of the di-2-thienylmethanone radical anion in dimethylformamide and acetonitrile at 293 K

Solvent	Conformer	$E_a/$ kJ mol ⁻¹	$\Delta H^\ddagger/$ kJ mol ⁻¹	$\Delta S^\ddagger/$ J mol ⁻¹ K ⁻¹	$\Delta G^\ddagger/$ kJ mol ⁻¹
HCONMe ₂	<i>trans,trans</i>	27.5	25.1	-43.8	37.9
	<i>cis,trans</i>	26.8	24.4	-44.8	37.5
MeCN	<i>trans,trans</i>	22.2	19.8	-55.0	35.9
	<i>cis,trans</i>	21.0	18.6	-58.2	35.7

**Figure 3.** The experimental e.s.r. spectrum of the phenyl-2-thienylmethanone radical anion, in dimethylformamide, at 293 K (A) together with its computer simulation (B) (parameters as given in Table 4)

methanone radical anion (at 293 K) is shown in Figure 3 together with its computer simulation. The various splitting constants required to obtain the best-fit computer simulations in each solvent are summarised in Table 4. The values of da/dT (see Table 5) are much greater for the thienyl ring than for the phenyl ring. This behaviour is very similar to that observed for the di-2-thienyl- and diphenyl-ethanedione radical anions: the values of da/dT were much smaller for the latter than for the former.¹ It is possible that the removal of spin density from the

Table 4. Hyperfine splitting constants (in μT) for the phenyl-2-thienylmethanone radical anion in dimethylformamide, acetonitrile, and dimethyl sulphoxide, obtained by best-fit computer simulation

T/K	$\alpha(3\text{-H})$	$\alpha(4\text{-H})$	$\alpha(5\text{-H})$	$\alpha(o\text{-H})$	$\alpha(m\text{-H})$	$\alpha(p\text{-H})$
Dimethylformamide						
233	454	(-) 107	418	233	(-) 76	310
243	455	(-) 107	419	233	(-) 76	310
253	451	(-) 106	415	232	(-) 76	309
263	449	(-) 105	413	231	(-) 76	308
273	447	(-) 105	411	231	(-) 76	308
293	441	(-) 104	405	230	(-) 76	306
313	441	(-) 104	405	230	(-) 76	306
333	440	(-) 104	404	230	(-) 76	306
353	440	(-) 104	404	230	(-) 76	306
Acetonitrile						
253	464	(-) 109	428	235	(-) 77	310
273	459	(-) 108	423	234	(-) 77	309
293	459	(-) 108	423	234	(-) 77	309
313	454	(-) 106	419	232	(-) 77	307
333	452	(-) 105	417	231	(-) 77	306
Dimethyl sulphoxide						
293	451	(-) 106	416	231	(-) 77	305

phenyl and thienyl rings reflects a change in the planarity of the ring with respect to the carbonyl system. Presumably this change is more pronounced for the thienyl than for the phenyl ring.

For both the radical anions reported in this paper the splitting constants are higher for a particular proton in acetonitrile than in dimethylformamide (at the same temperature). If the magnitude of the coupling reflects, at least to some extent, the planarity of the ring with respect to the carbonyl group, then presumably the rings are more planar in acetonitrile. Alternatively, however, solvation of the carbonyl group would be expected to influence the electronegativity of the carbonyl oxygen atom, this being reflected by a change in the total spin density in the rings.⁸

Table 5. Values of da/dT ($\times 10^2/\mu\text{T K}^{-1}$) for the phenyl-2-thienylmethanone radical anion in dimethylformamide and acetonitrile

	$da(3\text{-H})/dT$	$da(4\text{-H})/dT$	$da(5\text{-H})/dT$	$da(o\text{-H})/dT$	$da(m\text{-H})/dT$	$da(p\text{-H})/dT$
HCONMe ₂	-13.5	-2.7	-13.8	-2.7	0.0	-3.8
MeCN	-14.5	-5.0	-13.5	-5.0	0.0	-5.0

Generally, negative values of da/dT can be interpreted as resulting from a positive spin density on the proximate carbon atom.⁹ However, several of the values, notably $da(4\text{-H})/dT$ and $d(m\text{-H})/dT$, are small or zero. If the overall spin density is decreasing in the rings with an increase in temperature due to a change in planarity, these latter two values are consistent with negative spin densities. This conclusion is supported by the results for the similar ethanedione radical anions and by the results of molecular orbital calculations.¹

Acknowledgements

We thank the S.E.R.C. for a research studentship (to C. J. L.).

References

- C. J. Leach and B. J. Tabner, *J. Chem. Soc., Perkin Trans. 2*, 1985, 653.
- M. Guerra, G. F. Pedulli, M. Tiecco, and G. Martelli, *J. Chem. Soc., Perkin Trans. 2*, 1974, 562.
- H. D. Hartough and A. I. Kosak, *J. Am. Chem. Soc.*, 1947, **69**, 2098.
- C. H. Heathcock, L. G. Gulick, and T. Dehlinger, *J. Heterocycl. Chem.*, 1969, **6**, 141.
- B. J. Tabner and J. R. Zdysiewicz, *J. Chem. Soc., Perkin Trans. 2*, 1973, 811.
- R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.
- M. Branca, A. Gamba, M. Barzagli, and M. Simonetta, *J. Am. Chem. Soc.*, 1982, **104**, 6506.
- J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, 1962, **37**, 2832.
- P. D. Sullivan and E. M. Menger, *Adv. Magn. Reson.*, 1977, **9**, 1.

Received 10th May 1985; Paper 5/786