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

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The radical anions of di-2-furyl- (**1**) and 2-furyl-2-thienyl-methanone (**2**) have been prepared by electrochemical reduction in dimethylformamide, acetonitrile, and dimethyl sulphoxide. The e.s.r. spectrum of the former has been interpreted in terms of the presence of both *trans,trans*- and *cis,trans*-conformers and the activation parameters for the interconversion between these conformers have been determined. Individual conformers were not observed for the 2-furyl-2-thienylmethanone radical anion and the hyperfine splitting constants for this radical anion have been assigned by comparison with the appropriate parameters for the di-2-thienyl-, 2-phenyl-2-thienyl-, and di-2-furyl-methanone radical anions.

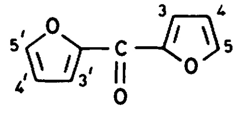
A detailed study of an e.s.r. spectrum over a range of temperatures can be extremely informative. For example, such a study of radical anions derived from planar aromatic hydrocarbons often reveals the sign of the hyperfine splitting constants.[1] In addition, however, important information can be obtained on various equilibria. Particularly interesting are spectra which exhibit linewidth effects arising from cation migration processes or conformational equilibria. We have recently reported an example of linewidths effects as a result of conformational equilibrium in the di-2-thienylmethanone radical anion in which both *trans,trans*- and *cis,trans*-conformers are present, but not the *cis,cis*-conformer.[2] In this latter system we also determined values of da/dT for each hyperfine splitting constant. These da/dT values are greater than normally expected for simple planar π-systems, indicating that the angle of twist of the ring system with respect to the carbonyl group varies with temperature or that the electronegativity of the carbonyl oxygen atom is temperature-dependent (possibly as a result of solvation effects).

We have now extended our study of these systems to include the di-2-furylmethanone radical anion prepared by electrochemical reduction in dimethylformamide. We have observed an equilibrium between rotational conformers in this system. We also report a study of the radical anion of 2-furyl-2-thienylmethanone, again prepared by electrochemical reduction in dimethylformamide. We are not aware of any previous report of this latter radical anion. We would expect the e.s.r. spectra of this radical anion to be rather complex, since there would be two different *cis,trans*-conformers [(B) and (C); Scheme]. However, no temperature-dependent linewidth phenomena were observed in this case.

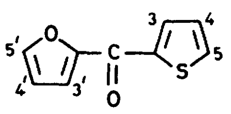
Experimental

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-furylmethanone was prepared by direct acylation of furan with furan-2-carboxylic acid.[3] The crude product was purified using a silica gel column and then distilled under reduced pressure. 2-Furyl-2-thienylmethanone was prepared by the addition of tin(IV) chloride to a solution of thiophene and 2-furoyl chloride in benzene.[4] The crude product was purified by distillation under reduced pressure.



(**1**)



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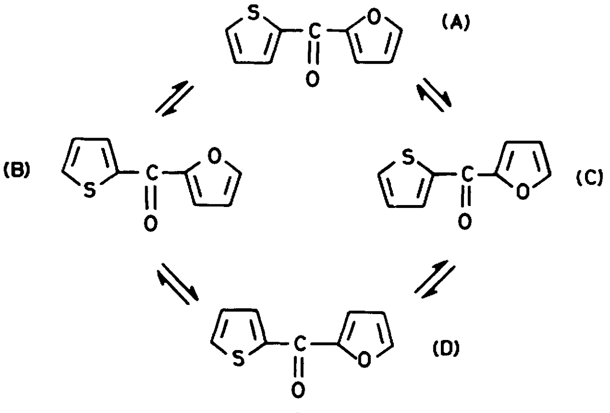

Scheme.

Procedure.—The concentrations of the solutions of the parent ketone, for electrochemical reduction, were in the range 1—3 × 10^{-3} mol l^{-1}, with tetra-n-butylammonium iodide (B.D.H.) as supporting electrolyte (0.1—0.2 mol l^{-1}). 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 salt[6] 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 appropriate program required for the simulation of the e.s.r. spectra of these radical anions is that for a four-jump model allowing for equilibria between the *cis,trans*-conformer and the *cis,cis*- and *trans,trans*-conformers. However, as explained later, in the di-2-furylmethanone radical anion only one of the two possible symmetric conformers contributed to the e.s.r. spectrum and the program employed, therefore, is based on the modified Bloch equations for a 'blocked' three-jump model (B) $\rightleftharpoons$ (A) $\rightleftharpoons$ (B).

The hyperfine splitting constants quoted from these simulations for the asymmetric (*cis,trans*-) conformer are considered

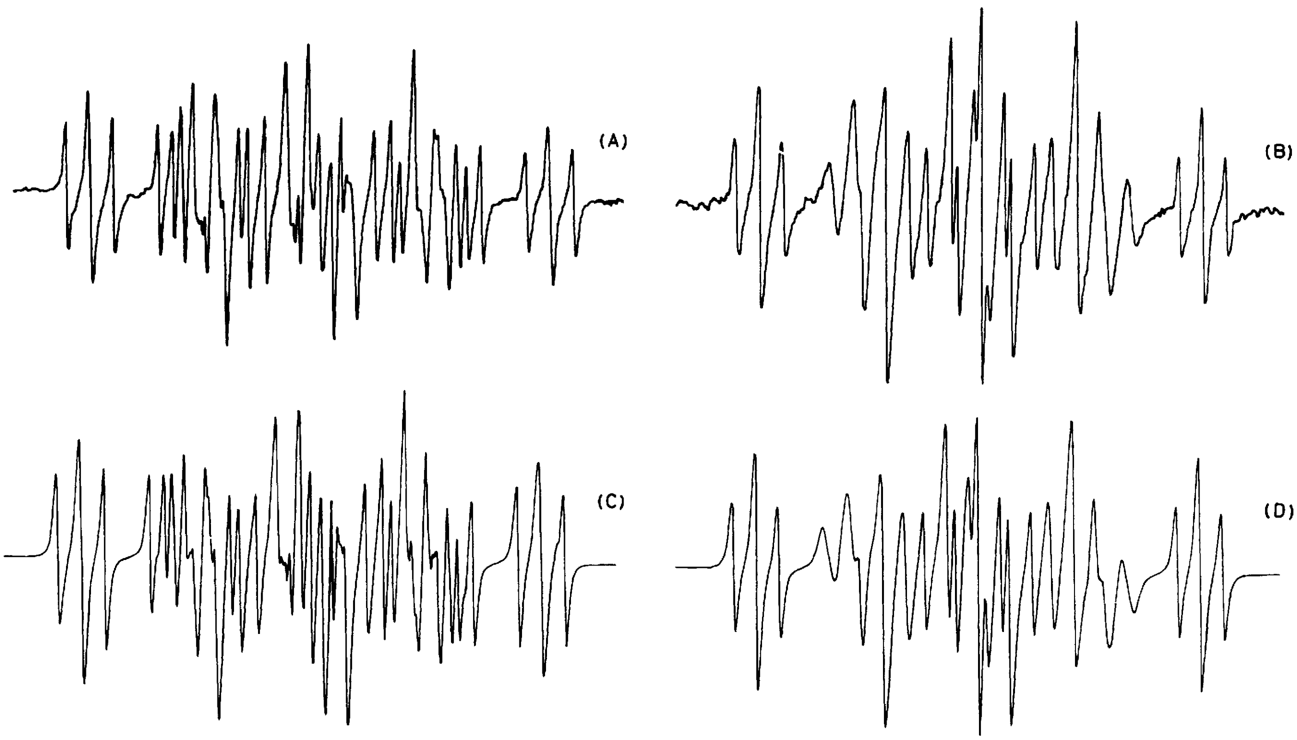

Figure 1. Experimental e.s.r. spectra of the di-2-furylmethanone radical anion, in dimethylformamide, at (A) 263 K and (B) 323 K, together with its computer simulation [(C) and (D) respectively; parameters as given in Table 1]

accurate to within ±1 μT. The corresponding temperature coefficients, d*a*/d*T*, obtained by a least-squares analysis, are considered accurate to within $\pm 1 \times 10^{-2}$ $\mu T\ K^{-1}$. However, the symmetric conformer makes only a minor contribution to the spectrum and the hyperfine parameters quoted for this conformer are correspondingly less accurate. The hyperfine parameters for the radical anion of 2-furyl-2-thienylmethanone have the same accuracy as for the asymmetric conformer of di-2-furylmethanone. (The absolute magnitude of *a* has been used to calculate the values of d*a*/d*T* quoted in this paper.)

Results and Discussion

Di-2-furylmethanone.—This ketone was reduced electrochemically, in all three solvents, to give a purple-blue solution of the radical anion. We describe first the e.s.r. spectra obtained in dimethylformamide. Spectra were recorded over the temperature range 243—333 K. Two features contrast with the corresponding spectra of the radical anion of di-2-thienylmethanone in the same solvent. First, in the di-2-thienylmethanone radical anion system the symmetric (*trans,trans-*) conformer was slightly more stable than the asymmetric (*cis,trans-*) conformer.[2] However, the reverse situation is observed in the di-2-furylmethanone radical anion system, with the asymmetric (*cis,trans-*) conformer considerably more stable than the symmetric (*trans,trans-* or *cis,cis-*) conformer. This situation leads to computer simulations which are sensitive to the hyperfine parameters and τ values of the *cis,trans*-conformer but are less sensitive to the corresponding values associated with the symmetric conformer. Secondly, in the spectrum of the di-2-thienylmethanone radical anion equivalence of the 4- and 4′-proton and of the 5- and 5′-proton led to a simplification of the computer simulations. In the di-2-furylmethanone radical anion, however, all six protons in the *cis,trans*-conformer are non-equivalent.

We again conclude that the symmetric conformer observed in this system is, in fact, the *trans,trans*-conformer. This assignment is based on the observations that the symmetric conformer has a higher *g* value than the *cis,trans*-conformer and also on the relative magnitudes of the 3-H splitting constants in the two conformers.[7]

The e.s.r. spectrum for this system at 263 K [Figure 1(A)] is slightly asymmetric. This feature is perhaps most obvious in the high-field and low-field end 'triplets'. On the other hand separate hyperfine lines attributable to two different conformers are not observed as was the case in the di-2-thienylmethanone radical anion.[2] However, attempts to simulate the spectrum in terms of a single species of constant linewidth failed and we were forced to the conclusion that the spectra require simulation in terms of two conformers (as already discussed) with lifetimes compatible with the e.s.r. timescale. 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 263 and 323 K, respectively]. 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.

The hyperfine splitting constants for both conformers are temperature-dependent (see Table 2 for values of d*a*/d*T* for each proton). However, the plots of *a vs. T* show no temperature-independent region as observed for the di-2-thienylmethanone radical anion in the same solvent.[2] The values of d*a*/d*T*, particularly at the 3- and 5-position, are much greater than normally observed for the radical anions derived from simple planar π-molecules.[1] This suggests that the angle of twist of the rings with respect to the carbonyl group is temperature-dependent (presumably increasing with temperature), although changes in solvation of the carbonyl group could result in similar effects.

Spectra of the radical anion were also recorded and computer-simulated over a temperature range in acetonitrile (253—333 K)

Table 1. Hyperfine splitting constants (in μT) for the di-2-furylmethanone 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})[a]

	trans,trans-Conformer				*cis,trans*-Conformer						
T/K	a(3-, 3′-H)	a(4-, 4′-H)	a(5-, 5′-H)	$10^8\tau_{tt}$/s	a(3-H)	a(3′-H)	a(4-H)	a(4′-H)	a(5-H)	a(5′-H)	$10^8\tau_{ct}$/s
Dimethylformamide											
243	465	(−)76	335	750	480	447	(−)88	(−)76	380	328	3 000
253	463	(−)76	333	560	479	446	(−)88	(−)76	379	327	2 250
263	462	(−)76	332	375	475	442	(−)88	(−)76	375	323	1 500
273	459	(−)75	329	50	474	441	(−)88	(−)76	375	322	200
283	458	(−)75	328	25	470	437	(−)88	(−)76	372	319	100
293	457	(−)75	327	12.5	469	436	(−)87	(−)76	371	318	50
303	456	(−)75	326	10	467	434	(−)87	(−)75	370	317	40
313	456	(−)75	326	5	467	434	(−)87	(−)75	370	317	25
323	454	(−)75	324	4	463	430	(−)87	(−)75	367	314	17.5
333	454	(−)75	324	2.5	463	430	(−)87	(−)75	367	314	10.
Acetonitrile											
253	482	(−)79	347	250	496	464	(−)90	(−)80	391	342	1 000
273	473	(−)79	338	25	489	457	(−)90	(−)80	385	336	100
293	468	(−)78	334	12.5	481	449	(−)89	(−)79	380	331	50
313	465	(−)78	332	6	477	445	(−)89	(−)79	376	327	25
333	460	(−)78	327	2.5	471	439	(−)89	(−)79	371	322	10
Dimethyl sulphoxide											
293	458	(−)75	328	12.5	471	438	(−)88	(−)76	375	322	50
333	454	(−)75	324	2.5	467	434	(−)88	(−)76	371	320	10

[a] Primes (′) refer to the *trans*-ring in the *cis,trans*-conformer.

Table 2. Values of $10^2(\mathrm{d}a/\mathrm{d}T)/\mu\mathrm{T\ K}^{-1}$ for each conformer of the di-2-furylmethanone radical anion in dimethylformamide and acetonitrile

	trans,trans-Conformer			*cis,trans*-Conformer					
Solvent	da(3-, 3′-H)/dT	da(4-, 4′-H)/dT	da(5-, 5′-H)/dT	da(3-H)/ dT	da(3′-H)/ dT	da(4-H)/ dT	da(4′-H)/ dT	da(5-H)/ dT	da(5′-H)/ dT
$HCONMe_2$	−12.2	−1.2	−12.2	−18.8	−18.8	−1.5	−1.5	−14.7	−15.6
MeCN	−26.0	−1.5	−23.0	−31.0	−31.0	−1.5	−1.5	−24.5	−24.5

and at two temperatures in dimethyl sulphoxide. The procedure used for the radical anion in dimethylformamide was followed in order to obtain the results reported in Table 1. As can be seen the *cis,trans*-conformer predominates over the *trans,trans*-conformer in all three solvents. It is interesting that each hyperfine splitting constant (in both conformers) is greater, at a particular temperature, in acetonitrile than in dimethylformamide. Presumably this is a consequence of differences in solvation leading either to greater planarity in acetonitrile or to specific solvation of the carbonyl group in acetonitrile resulting in a greater transfer of spin density to the furyl rings. Although results at only two temperatures are available for dimethyl sulphoxide these provide an interesting comparison. For the *trans,trans*-conformer the splitting constants, at a particular temperature, in this solvent are virtually identical with the values in dimethylformamide. However for the *cis,trans*-conformer the splitting constants in both rings are greater in dimethyl sulphoxide than in dimethylformamide. This observation indicates the specific nature of solvation effects, with one conformer more sensitive to a change of solvent than the other. The values of da/dT at each position also show an interesting insight into these effects (see Table 2). Both in dimethylformamide and in acetonitrile the values of da/dT at each position are greater for the *cis,trans*-conformer than for the *trans,trans*-conformer and are greater for both conformers in acetonitrile than in dimethylformamide. This contrasts markedly with the results obtained for the di-2-thienylmethanone radical anion; in this case, over the temperature range 293—353 K, the da/dT values were virtually the same for a particular position in both conformers and in both solvents.[2]

The lifetime (τ) of the two conformers obtained from the best-fit computer simulations are also quoted in Table 1. As can be seen, the *cis,trans*-conformer of the di-2-furylmethanone radical anion has the greater lifetime, at any particular temperature, in all three solvents. This is the reverse of the situation observed for the di-2-thienylmethanone radical anion; here the *trans,trans*-conformer has the greatest lifetime in all three solvents.[2] However, the radical anion of di-2-thienylmethanone has also been studied in a sodium methoxide–methanol–dimethoxyethane (1:3:4).[7] In this medium the *cis,trans*-conformer has the greatest lifetime. These comparisons show the importance of solvation in determining the relative lifetimes of the various conformers of these radical anions.

In all cases a good linear Arrhenius plot (ln k *vs.* $1/T$) was obtained; the activation energies for the interconversion between the conformers in dimethylformamide and acetonitrile are summarised in Table 3. The activation energies for the interconversion of the two conformers, in a particular solvent, are within experimental error. The activation energies are, however, greater in dimethylformamide than in acetonitrile. This feature was also observed for the di-2-thienylmethanone radical anion.[2] Table 3 also summarises the various values of $\Delta G^‡$, $\Delta H^‡$, and $\Delta S^‡$. Both in dimethylformamide and in acetonitrile, a more positive $\Delta S^‡$ is observed for conversion of

Table 3. Activation parameters for conversion of each conformer of the di-2-furylmethanone radical anion into the other in dimethylformamide and acetonitrile

Solvent	Starting 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}
$HCONMe_2$	*trans,trans*	36.8	34.4	4.8	33.0
	cis,trans	35.7	33.3	−18.3	38.7
MeCN	*trans,trans*	28.7	26.3	−22.4	32.9
	cis,trans	28.5	26.1	−40.2	37.9

Table 4. Hyperfine splitting constants (in μT) for the radical anions of di-2-thienyl-, of 2-phenyl-2-thienyl-, and of di-2-furyl-methanone in dimethylformamide at 273 K, obtained by best-fit computer simulations, together with the corresponding *a*(5-H)/*a*(3-H) and *a*(4-H)/*a*(3-H) values

Radical anion		*a*(3-H)	*a*(4-H)	*a*(5-H)	*a*(5-H)/*a*(3-H)	*a*(4-H)/*a*(3-H)
Di-2-thienylmethanone						
trans,trans-Conformer		418	(−)93	372	0.89	0.22
cis,trans-Conformer	*cis*-Ring	436	(−)95	376	0.86	0.22
	trans-Ring	425	(−)95	376	0.88	0.22
2-Phenyl-2-thienylmethanone		447	(−)105	411	0.91	0.23
Di-2-furylmethanone		459	(−)75	329	0.72	0.16
trans,trans-Conformer		474	(−)88	375	0.79	0.19
cis,trans-Conformer	*cis*-Ring	441	(−)76	322	0.73	0.17
	trans-Ring					
2-Furyl-2-thienylmethanone						
	Thienyl ring	498	(−)108	456	0.92	0.22
	Furyl ring	393	(−)67	277	0.70	0.17

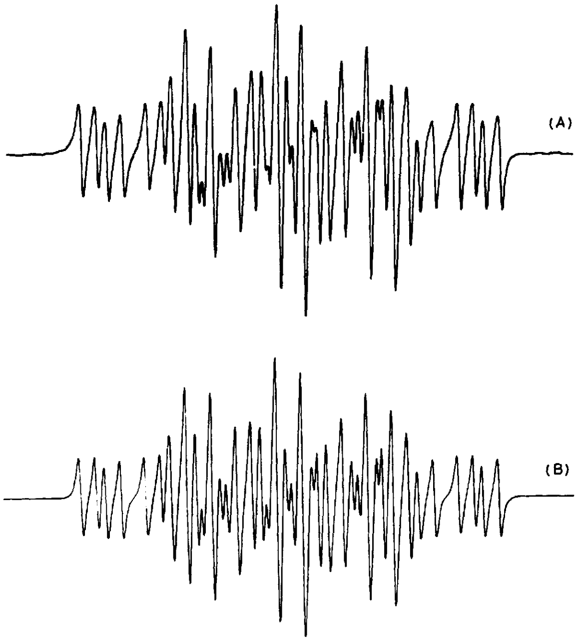

Figure 2. Experimental e.s.r. spectrum (A) of the 2-furyl-2-thienylmethanone radical anion, in dimethylformamide, at 223 K (A), together with its computer simulation (B); parameters as given in Table 5

the *trans,trans*-conformer into the *cis,trans*-conformer than for the reverse conversion. Since, in a particular solvent, $\Delta H^{\ddagger}$ is essentially the same for both conversions, this appears to reflect a change in solvation environment, probably in the vicinity of the carbonyl group, in moving from one conformer to the other. It is apparent, therefore, that it is this change in the value of $\Delta S^{\ddagger}$ for the conversion of the *trans,trans*-conformer relative to the conversion of the *cis,trans*-conformer which is responsible for the enhanced stability of the *cis,trans*-conformer of the di-2-furylmethanone radical anion relative to the di-2-thienylmethanone radical anion.

2-*Furyl*-2-*thienylmethanone*.—This ketone was readily reduced electrochemically, in all three solvents, to give a green solution of the radical anion. E.s.r. spectra were recorded over a wide temperature range in both dimethylformamide (223—293 K) and acetonitrile (243—313 K). We expected some degree of complexity in the e.s.r. spectra of this radical anion as two symmetric conformers [(B) and (C); Scheme] are possible in addition to the *cis,cis*- and *trans,trans*-conformers. However, the spectra show no evidence of linewidth variation and can be readily simulated in terms of a single species. A typical simulation, of the spectrum in dimethylformamide at 223 K, is shown in Figure 2; it requires six single proton splitting constants (506, 464, 401, 283, 109, and 68 μT).

We have assigned the hyperfine splitting constants to the 3-, 4-, and 5-protons in the furyl and thienyl rings by comparing their relative magnitudes with *a*(5-H)/*a*(3-H) and *a*(4-H)/*a*(3-H) observed in the spectra of the radical anions of di-2-thienylmethanone, 2-phenyl-2-thienylmethanone, and di-2-furylmethanone in dimethylformamide at 273 K (see Table 4). The relevant values of these splitting constants for the 2-furyl-2-thienylmethanone radical anion in this solvent at this temperature are 498, 456, 393, 277, 108, and 67 μT. It is clear that the two smallest values (108 and 67 μT) can be assigned to the 4-position. The ratio of the largest splitting constant (498 μT) to the 277 μT splitting constant is 0.56:1. Since this ratio is substantially different from any of those for either ring in any of the other radical anions (see Table 4) we have assigned these two splitting constants to different rings. The 277 and 456 μT splitting constants have a ratio of 0.61:1, again substantially different from the ratios in Table 4. These two values are therefore also assigned to different rings. This indicates that the 393 μT splitting constant should be assigned to the same ring as the 277 μT splitting constant and the 498 μT splitting constant to the same ring as the 456 μT splitting constant. These splitting constants have ratios of 0.70:1 and 0.92:1, respectively, and are

Table 5. Hyperfine splitting constants (in μT) for the 2-furyl-2-thienylmethanone radical anion in dimethylformamide, acetonitrile, and dimethyl sulphoxide, obtained by best-fit computer simulation[a]

T/K	*a*(3-H)	*a*(3′-H)	*a*(4-H)	*a*(4′-H)	*a*(5-H)	*a*(5′-H)
Dimethylformamide						
223	506	401	(−)109	(−)68	464	283
233	505	400	(−)108	(−)67	463	282
243	501	397	(−)108	(−)67	459	280
253	498	393	(−)107	(−)66	455	276
263	498	394	(−)108	(−)67	456	277
273	498	393	(−)108	(−)67	456	277
283	498	393	(−)108	(−)67	455	276
293	498	393	(−)108	(−)67	455	276
Acetonitrile						
243	513	414	(−)114	(−)71	462	306
253	512	415	(−)114	(−)71	462	306
263	511	413	(−)114	(−)71	459	305
273	508	409	(−)113	(−)70	454	303
283	505	407	(−)113	(−)70	452	302
293	503	404	(−)113	(−)70	449	301
313	501	401	(−)112	(−)70	446	300
Dimethyl sulphoxide						
293	495	390	(−)107	(−)68	449	278

[a] Primes (′) refer to the furyl ring.

Table 6. Values of $10^2(\mathrm{d}a/\mathrm{d}T)/\mu\mathrm{T\,K^{-1}}$ for each conformer of the 2-furyl-2-thienylmethanone radical anion in dimethylformamide and acetonitrile

	Furyl ring			Thienyl ring		
Solvent	d*a*(3′-H)/d*T*	d*a*(4′-H)/d*T*	d*a*(5′-H)/d*T*	d*a*(3-H)/d*T*	d*a*(4-H)/d*T*	d*a*(5-H)/d*T*
$HCONMe_2$	−12.1	−0.7	−10.4	−11.9	−0.7	−13.2
MeCN	−21.5	−1.8	−9.8	−19.1	−2.9	−25.8

assigned to the furyl and thienyl rings, respectively, by comparison with the other appropriate ratios in Table 4. The two smallest splitting constants, 108 and 67 μT, are assigned to the thienyl and furyl rings, respectively, again by comparison with the other appropriate ratios in Table 4. These assignments are summarised in Table 4.

The various splitting constants required to obtain the best-fit computer simulations in each solvent are summarised in Table 5, and the corresponding d*a*/*T* values in Table 6. Table 5 shows that the splitting constants at a particular position are greater, at the same temperature, in acetonitrile than in dimethylformamide. This feature is common to the di-2-thienyl- and 2-phenyl-2-thienyl-methanone radical anions,[2] reflecting either greater planarity with respect to the carbonyl group in the former solvent or the influence of solvation of the carbonyl group on the electronegativity of the carbonyl oxygen atom. The values of d*a*/d*T* are also greater in acetonitrile than in dimethylformamide with the curious exception of d*a*(5′-H)/d*T*.

It is perhaps surprising that, although linewidth alternation is observed in the e.s.r. spectra of the radical anions of di-2-thienyl-[2] and di-2-furyl-methanone, it is not observed in the spectrum of the radical anion of 2-furyl-2-thienylmethanone over the same temperature range. This latter spectrum is readily interpreted in terms of a single species; consequently there are two explanations of this feature. First, one of the four possible conformers is significantly more stable than the other three conformers and hence predominates or, secondly, two (or more) conformers are present but are interconverting rapidly on the timescale of the e.s.r. experiment. Unfortunately it is not possible to distinguish between these alternatives.

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