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

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The radical anions of di-2-furanyl-, bis-2-(5-methylfuranyl)-, di-2-thienyl-, di-2-pyrrolyl-, and diphenyl-ethanediones have been prepared by electrochemical reduction in dimethylformamide, dimethyl sulphoxide, and acetonitrile. Their e.s.r. spectra have been recorded and interpreted over a wide temperature range and the temperature dependence of the various hyperfine splitting constants obtained. The spectra of the heterocyclic ethanedione radical anions are asymmetric at low temperature possibly as a result of equilibration between various conformers. The temperature dependence of the hyperfine splitting constants of these radical anions is linear, but is much greater for those of the heterocyclic ethanediones than for diphenylethanedione.

The temperature dependence of hyperfine splitting constants in e.s.r. spectra can often reveal important information.[1] The most striking examples are perhaps the temperature-dependent hyperfine splitting constants associated with alkali-metal ions in ion pairs when the radical anion has been prepared by alkali-metal reduction.[2,3] In comparison with that observed for alkali-metal ions the temperature dependence of proton (and other magnetic nuclei) hyperfine splitting is usually small. In many cases this latter temperature dependence can be understood in terms of changes in the π-electron distribution resulting from changes in the environment of the alkali-metal ion. It is often informative, therefore, to study the temperature dependence of hyperfine splitting constants in the absence of alkali-metal ion interactions by preparing the radical anions by electrochemical reduction in a solvent such as dimethylformamide. The origin of the temperature dependence can lie in vibrational or rotational motions, or in the shift in position of an equilibrium.[1] The sign of the temperature coefficient is also helpful in predicting the sign of hyperfine splitting constants.[4,5]

In this paper we report the results of a detailed investigation of the temperature dependence of the hyperfine splitting constants in the di-2-furanyl- and di-2-thienyl-ethanedione radical anions prepared by electrochemical reduction in dimethylformamide. These radical anions are well suited to a detailed investigation of the influence of temperature due to the relative simplicity of their spectra. Measurements have also been made in acetonitrile and dimethyl sulphoxide in order to obtain information on the influence of solvent on the hyperfine splitting constants. The results of measurements on the diphenylethanedione radical anion have been included for the purpose of comparison. We also report the results of a study of the e.s.r. spectrum of the radical anion of di-2-pyrrolylethanedione again prepared by electrochemical reduction in dimethylformamide and acetonitrile.

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 4A molecular sieve.

Di-2-thienylethanedione was prepared from thiophene-2-carbaldehyde (Aldrich) as described[6] and purified by recrystallisation from ethanol, (m.p. 82—83 °C). The purity of the product was checked by i.r. and n.m.r. spectroscopy. Bis-2-(5-methylfuranyl)ethanedione was similarly prepared from 2-(5-methylfuran)carbaldehyde (Aldrich). Both di-2-furanylethanedione and diphenylethanedione (both Aldrich) were purified by recrystallisation from methanol before use. The sample of di-2-pyrrolylethanedione used in these experiments was the generous gift of Dr. S. Brandange (Arrhenius Laboratory, University of Stockholm) and had been purified by sublimation and recrystallisation from methanol.

Procedure.—Solutions of the ethanediones for electrochemical reduction were normally 1×10^{-3} mol dm^{-3} with 0.1 mol dm^{-3} tetra-n-butylammonium iodide (B.D.H.) as supporting electrolyte. Solutions of the radical anions were prepared for e.s.r. study as described.[7]

Spectroscopic Measurements.—E.s.r. spectra were recorded on a Varian E3 spectrometer. The magnetic field sweep was calibrated using Fremy's salt[8] 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 computer on line to the spectrometer or on an ICL 1905E computer linked to a Calcomp plotter. The hyperfine splitting constants quoted from these simulations are considered accurate to ± 1 μT. The temperature coefficients, $\mathrm{d}a/\mathrm{d}T$, for the variation in the hyperfine splitting constants with temperature have been obtained by a least-squares analysis and are considered accurate to $\pm 1.0 \times 10^{-2}$ μT K^{-1}. (The absolute magnitude of a has been used to calculate the values of $\mathrm{d}a/\mathrm{d}T$ quoted in this paper.)

Molecular Orbital Calculations.—Molecular orbital calculations were performed with the aid of the ICL computer.

Results and Discussion

Di-2-furanylethanedione (Furil).—This dione was readily reduced electrochemically in all three solvents to give a blue solution of the radical anion. The spectrum of the radical anion, readily interpreted in terms of three pairs of two equivalent protons, was recorded at 20° intervals from 213 to 333 K in dimethylformamide and a computer simulation obtained for each spectrum. The resulting hyperfine splitting constants are quoted in Table 1 and agree well with those previously reported at 298 K.[9] A typical spectrum, that at 253 K, and its computer simulation are illustrated in Figure 1.

Slight discrepancies between the experimental and simulated spectra were observed in that the lines on the high-field side of the spectrum were generally less intense than their low-field counterparts. Additionally the relative intensities of the low- and high-field end triplets, arising from the smallest of the

Table 1. Hyperfine splitting constants (in μT) for the di-2-furanylethanedione radical anion in dimethylformamide

T/K	a(3-H)	a(4-H)	a(5-H)
213	208	(−)35	155
233	207	(−)35	154
253	206	(−)35	153
273	203	(−)35	152
293	201	(−)35	150
313	199	(−)34	148
333	198	(−)34	147

Figure 1. The experimental e.s.r. spectrum of the di-2-furanylethanedione radical anion, in dimethylformamide, at 253 K (A) together with its computer simulation (B) (parameters as given in Table 1)

splitting constants, were also asymmetric with the high-field line in both of these triplets having a greater intensity than its low-field counterpart. However, these discrepancies become less obvious with increasing temperature.

Hückel molecular orbital calculations, particularly when used with McLachlan modification, have proved invaluable in assigning hyperfine splitting constants to particular protons in a wide range of radical anions.[10] There is little doubt that the smallest of the three values can be assigned to 4-H but in order to assign the remaining values a series of molecular orbital calculations were undertaken. The problem here, however, lies in the number of variable parameters involved when the radical anion contains heteroatoms. Two parameters, k_{CX} and h_X [see equations (1) and (2)] are required for each heteroatom, and a

$$\beta_{CX} = k_{CX}\beta_{CC} \qquad (1)$$

$$\alpha_X = \alpha_C + h_X\beta_{CC} \qquad (2)$$

further variable parameter k_{CC} is required to allow for the nonplanarity of the rings with respect to the carbonyl groups.[11] The values of k_{CO} and h_O for the carbonyl oxygens were selected as 1.6 and 1.5, respectively. These values have been optimised for the benzophenone[12] and some benzoylpyridine[13] radical anions and were found to be satisfactory for the diphenylethanedione radical anion (see later). The appropriate values of the parameters for the furanyl oxygens, however, presents a greater problem. Calculations employing some previously successful values[11,14,15] (with the McConnell parameter $|Q| = 2.4$ mT and the McLachlan parameter $\lambda = 1$) predicted virtually identical splitting constants for 3- and 5-H.

Table 2. Hyperfine splitting constants (in μT) for the bis-2-(5-methylfuranyl)ethanedione radical anion in dimethylformamide

T/K	a(3-H)	a(4-H)	a(5-H)[a]
233	226	(−)31	161
253	225	(−)31	160
273	223	(−)31	158
293	222	(−)31	156
313	220	(−)30	154
333	219	(−)30	153

[a] Two equivalent methyl groups.

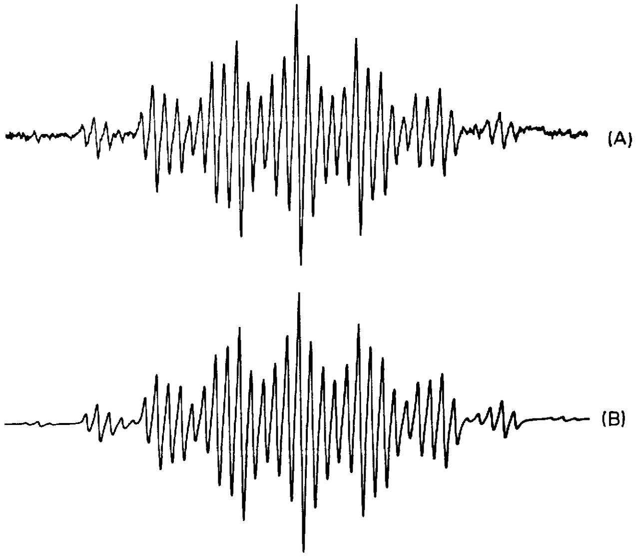


Figure 2. The experimental e.s.r. spectrum of the bis-2-(5-methylfuranyl)ethanedione radical anion, in dimethylformamide, at 253 K (A) together with its computer simulation (B) (parameters as given in Table 2)

The variation of h_O also led to a reversal of the assignment at these two positions. The best-fit parameters were found to be $h_O = k_{CO} = 1$ and with the k_{CC} parameter also unity, suggesting that the furanyl rings are coplanar with the carbonyl system. (This, in fact, would seem rather unlikely.) These best-fit values were 207, −32, and 142 μT for the 3-, 4-, and 5-H, respectively.

In view of the difficulty experienced in making a conclusive assignment by this approach the radical anions of some substituted di-2-furanylethanediones were considered. Selective deuteriation seems a good possibility. However proton–deuterion exchange appears to occur readily during electrochemical reduction.[16] The alternative approach involves t-butyl or methyl substitution, where perturbation of the π-electron distribution by the substituent is generally small.[17,18]

Bis-2-(5-*methylfuranyl*)*ethanedione*.—The radical anion of this dione was readily obtained by electrochemical reduction in all three solvents. Again the e.s.r. spectrum is readily interpreted, this time in terms of two sets of two equivalent protons and one set of six equivalent protons. Spectra were recorded at 20° intervals from 233 to 333 K in dimethylformamide and a typical spectrum (that at 253 K) is illustrated in Figure 2 together with its computer simulation. The splitting constants are readily assigned in this radical anion (see (Table 2) and confirm that in the di-2-furanylethanedione radical anion the largest splitting constant should be assigned to 3-H. These results confirm that

Table 3. Hyperfine splitting constants (in μT) for the di-2-thienylethanedione radical anion in dimethylformamide

T/K	a(3-H)	a(4-H)	a(5-H)
233	206	(−)39	163
253	205	(−)39	162
273	204	(−)39	160
293	203	(−)39	159
313	201	(−)39	158
333	199	(−)39	157

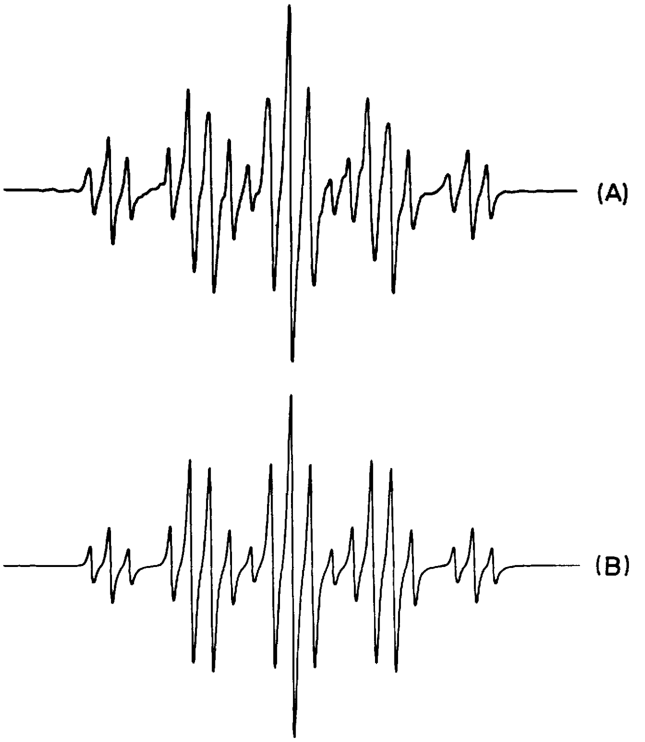


Figure 3. The experimental e.s.r. spectrum of the di-2-thienylethanedione radical anion, in dimethylformamide, at 233 K (A) together with its computer simulation (B) (parameters as given in Table 3)

methyl substitution results in only a minor perturbation of the π-electron distribution, leading to a small increase at the 3-position and a small decrease at the 4-position.

Di-2-thienylethanedione (*Thenil*).—This dione was again readily reduced electrochemically in all three solvents to give a green solution of the corresponding radical anion. Spectra, in dimethylformamide, were recorded at 20° intervals over the temperature range 233 to 333 K and are readily interpreted in terms of the three expected sets of two equivalent protons. A typical spectrum, that at 233 K, together with its computer simulation, is illustrated in Figure 3 and the hyperfine splitting constants at each temperature are summarised in Table 3 and again agree well with those previously reported at 298 K.[9] As with the di-2-furanylethanedione radical anion the relative intensities of corresponding high- and low-field lines were asymmetric. This feature was rather more pronounced than in the former radical anion, but took the same form. That is the corresponding high-field lines were less intense than their low-field counterparts but within the end triplet the high-field line was more intense than its low-field counterpart. Again, this asymmetry decreases with increasing temperature.

The assignment of the splitting constants to the various protons in the thienyl ring has been based upon those established above for the furanyl ring. The parameters usually employed for the sulphur atom in molecular orbital calculations are similar to those for the oxygen atom[11] and consequently the resulting calculations result in similar conclusions to those for the furanyl ring. It seems unlikely that the assignments to the 3- and 5-positions would be reversed in the two heterocyclic rings and the similarity in the absolute values of all three splitting constants suggests that the same assignments are appropriate.

Table 4. Hyperfine splitting constants (in μT) for the di-2-pyrrolylethanedione radical anion in dimethylformamide

T/K	a(N)	a(H-N)	a(2-H)	a(3-H)	a(4-H)
233	17	<4	173	(−)40	132
253	17	<4	172	(−)40	131
273	18	<4	171	(−)40	130

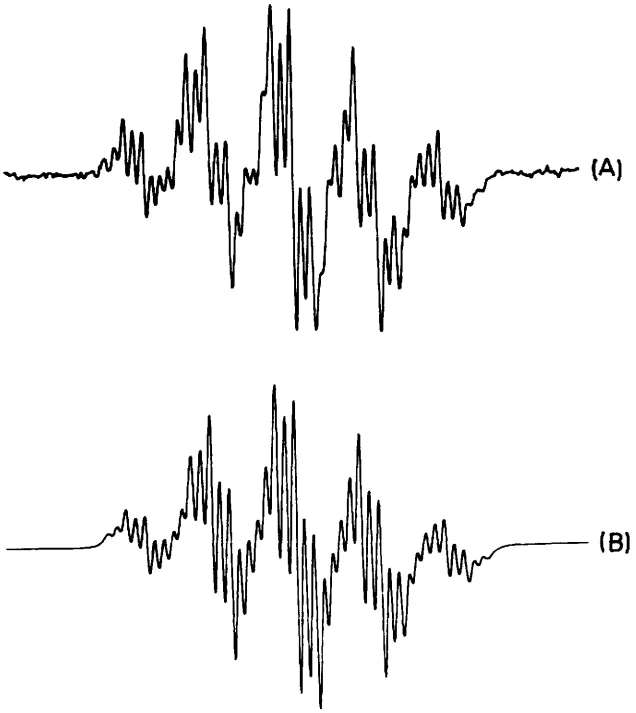


Figure 4. Experimental e.s.r. spectrum of the di-2-pyrrolylethanedione radical anion, in dimethylformamide, at 253 K (A) together with its computer simulation (B) (parameters as given in Table 4)

Di-2-pyrrolylethanedione.—This dione was found to be difficult to reduce and gave spectra of relatively low intensity. Spectra were again recorded at 20° intervals from 233 to 333 K in dimethylformamide but those at 293 K and above were of poor resolution. However, it was possible, with the aid of computer simulations, to interpret the spectra obtained at the three lowest temperatures in terms of coupling to three sets of two equivalent protons and to one set of two equivalent nitrogen atoms. However, hyperfine coupling to the NH protons was not observed within the linewidth of the spectrum and it is possible that this radical anion exists as the corresponding deprotonated structure.[19] The spectrum recorded at 253 K, together with its computer simulation, is illustrated in Figure 4 and the hyperfine splitting constants obtained from the computer simulations are summarised in Table 4.

Table 5. Hyperfine splitting constants (in μT) for the diphenylethanedione radical anion in dimethylformamide

T/K	a(o-H)	a(m-H)	a(p-H)
233	100	(−)36	112
253	99	(−)36	112
273	99	(−)36	111
293	98	(−)36	110
313	98	(−)36	110
333	98	(−)36	110
Calculated[a]	98	−30	112

[a] $|Q|$ = 2.4 mT, λ = 1.0.

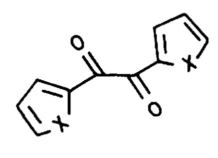
The assignment of the various splitting constants to the ring protons has been based on the assignments for the di-2-furanyl- and di-2-thienyl-ethanedione radical anions.

Diphenylethanedione.—Although the radical anion of this dione has been prepared by electrochemical reduction previously[20] it has been included in the present study in order to compare the temperature dependence of the hyperfine splitting constants in dimethylformamide with those for the heterocyclic diones reported above. Again e.s.r. spectra were recorded at 20° intervals from 233 to 333 K and the splitting constants obtained from the best-fit computer simulations are summarised in Table 5. The calculated splitting constants quoted in Table 5 have been obtained using the values 1.6 and 1.5 for k_{CO} and h_O, respectively. The best-fit values also require a value of 0.75 for the k_{CC} parameter suggesting an angle of twist of the phenyl rings with respect to the carbonyl system of *ca.* 40°.

Temperature Dependence of Hyperfine Splitting Constants.—One possible explanation of the observed temperature dependence of the hyperfine splitting constants in these dione radical anions could be a shift in equilibrium position between various conformers with temperature. There are six possible conformers for each of the heterocyclic dione radical anions studied. If the g-value and splitting constants varied slightly from conformer to conformer, as might be expected, the observed temperature dependence could be anticipated if all six conformers were rapidly interconverting and the overall position of the equilibrium shifted with temperature.

The conformers can be split into two groups, those with the carbonyl groups *trans* with respect to each other [(**1**)—(**3**)] and those with the carbonyl groups *cis* with respect to each other (**4**)—(**6**). It is unlikely, however, that these two sets of conformers will be equally stable. The magnitude of the splitting constants indicates a large unpaired electron density on the carbonyl groups, a conclusion supported by molecular orbital calculations, and the resulting electronic repulsion between the electronegative oxygen atoms would favour the *trans*-conformers. There is experimental evidence in other diones to support this conclusion. For example, Russell *et al.* have found that in the butane-2,3-dione radical anion the *cis*:*trans* ratio varies with counterion and solvent.[21,22] However, in the case of the 'free' ion only the *trans*-conformer was observed, the *cis* conformer only being present when 'trapped out' by an alkali-metal ion in an ion pair.

The observed temperature dependence in our spectra could be explained by rapid equilibration between two or three of the *trans*-conformers, and by the position of the equilibrium shifting with temperature to favour different conformers. Such an explanation would be convenient in that it would explain the relatively high values of da/dT observed in these radical anions and also the lack of symmetry in the line intensities. However there is important additional experimental information. In the e.s.r. sepctra of the corresponding methanone radical anions the hyperfine splitting constants of each individual conformer can be determined and these values are also found to vary significantly with temperature.[23] While it is still quite possible that a shift in equilibrium position could explain the observed temperature dependence, an alternative explanation therefore appears possible.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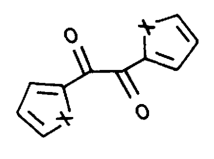
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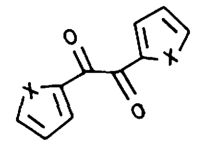
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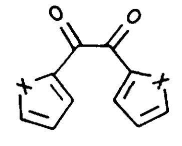
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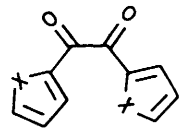
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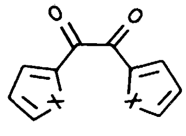
(6)

X = O, S, or NH

An alternative possible explanation for the observed asymmetry in the relative line intensities could lie in the sign of the splitting constants. The high-field spectral lines might be expected to be broader if there is a positive spin density on the proximate ring carbon atom, and narrower if there is a negative spin density on the carbon atom.[4,5,24] Linewidth asymmetries, therefore, provide criteria by which the signs of hyperfine splitting constants can be determined. In many spectra this information is generally difficult to obtain due to the large number of overlapping hyperfine components. However, the present spectra are relatively straightforward with little overlap and the sign of da/dT should, in principle, indicate the sign of the splitting constant. The various temperature coefficients are summarised in Table 6.

The negative values of da/dT for 3- and 5-H in the heterocyclic ethanedione radical anions (and for the o- and p-H for the diphenylethanedione radical anion) indicate, as would be expected, a positive spin density on the proximate carbon atom. The values of da(4-H)/dT and da(m-H)/dT are, however much smaller and close to zero. The comparatively large da/dT values could well indicate a change in coplanarity of the ring with respect to the carbonyl system corresponding to a greater localisation of the unpaired electron density on the carbonyl system at higher temperatures. If this is the case, and the overall unpaired electron density is increasing in the rings as the temperature decreases, then the values of da(4-H)/dT and da(m-H)/dT would be consistent with negative spin densities on the proximate carbon atoms.

The hyperfine splitting constants of the radical anions were also measured in acetonitrile and dimethyl sulphoxide. The results of these measurements are collected in Table 7; it should be noted that the comparison between dimethylformamide and

Table 6. Values of da/dT ($\times 10^2$/μT K^{-1}) for each of the ethanedione radical anions in dimethylformamide

Ethanedione	da(3-H)/dT	da(4-H)/dT	da(5-H)/dT	da(N)/dT
Di-2-furanyl	−9.7	−1.1	−7.4	
Bis-2-(5-methylfuranyl)	−7.2	−1.1	−8.6	
Di-2-thienyl	−6.9	0.0	−6.1	
Di-2-pyrrolyl	−5.0	0.0	−5.0	2.5
	da(o-H)/dT	da(m-H)/dT	da(p-H)/dT	
Diphenyl	−1.8	0.0	−2.1	

Table 7. A comparison of hyperfine splitting constants (in μT) for each ethanedione radical anion in dimethylformamide, dimethyl sulphoxide, and acetonitrile

Ethanedione	Position	$HCONMe_2$–Me_2SO [a]	$HCONMe_2$–MeCN [b]
Di-2-furanyl	3	201:202	206:211
	4	(−)35:(−)35	(−)35:(−)35
	5	150:149	153:158
Bis-2-(5-methylfuranyl)	3	222:216	225:229
	4	(−)31:(−)32	(−)31:(−)33
	5	156:153	160:162
Di-2-thienyl	3	203:202	205:208
	4	(−)39:(−)40	(−)39:(−)40
	5	159:160	162:167
Di-2-pyrrolyl	1*		17:19
	3		172:175
	4		(−)40:(−)38
	5		131:137
Diphenyl	o	98:98	99:97
	m	(−)36:(−)36	(−)36:(−)36
	p	110:111	112:109

* Hyperfine coupling to ^{14}N.

[a] At 293 K. [b] At 253 K.

dimethyl sulphoxide is made at 293 K, and that between dimethylformamide and acetonitrile at 253 K. In general the comparisons show that the values in dimethylformamide and dimethyl sulphoxide are fairly similar, but that those in dimethylformamide and acetonitrile are significantly different. In the latter comparison the values of the hyperfine splitting constants are greater in acetonitrile with the exception of the diphenylethanedione radical anion where the values are smaller in acetonitrile.

A possible mechanism for the solvent dependence of hyperfine splitting constants, in which the solvent interacts with the polar sites within the radical anion, has been proposed.[25] A good example of this can be seen in the ^{14}N coupling in the nitrobenzene radical anion which varies markedly with solvent, whereas the ring splitting varies only slightly.[25,26] Similarly, it has been shown that the carbonyl groups in the benzoquinone radical anion are important solvation sites. Here the value of $a(^{13}C)$ for the carbonyl carbon atom varies from 213 to 65 μT in changing from dimethyl sulphoxide to a dimethyl sulphoxide–water mixture, with a corresponding change in the proton splitting constant from 242 to 239 μT.[25,27]

In the ethanedione radical anions studied, with the exception of that of diphenylethanedione, the rings themselves contain electronegative substituents, thus providing additional solvation sites. This feature may well explain the different behaviour of this radical anion. There are two possible explanations for the overall change in the electron density in the rings. First, it has been proposed that the solvation of the carbonyl groups can influence the electronegativity of the carbonyl oxygen atom, thereby modifying the spin density.[25] Secondly, it is possible that the solvation influences the relative rotation of the rings with respect to the carbonyl system, thus again modifying the spin density.

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