An Electron Spin Resonance Investigation of the 2-Pivaloyl-1,4-benzoquinone Radical Anion

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The 2-pivaloyl-1,4-benzoquinone radical anion has been prepared both by electrochemical reduction (in dimethylformamide) and by alkali-metal reduction (in tetrahydrofuran). The e.s.r. spectrum observed in dimethylformamide is that of a single species. However, in tetrahydrofuran the nature of the spectra depend on the alkali-metal counter-ion. For example, linewidth variation is observed when K^+ is the counter-ion whilst two separate species are observed when Li^+ is the counter-ion. The results of these experiments indicate that the various species result from different locations of the alkali-metal counter-ion adjacent to the radical anion rather than from rotational conformers resulting from the rotation of the pivaloyl group.

The radical anions of benzoquinones are usually very stable with well resolved e.s.r. spectra. When these radical anions are prepared by alkali-metal reduction, the alkali-metal counter-ion can migrate between the two equivalent sites adjacent to the carbonyl groups. If the rate of this migration is compatible with the timescale of the e.s.r. experiment linewidth variations are observed in their spectra. Such is the case in the 1,4-benzoquinone radical anion itself,[1-3] in a number of disubstituted 1,4-benzoquinones,[4-7] and in 1,4-naphthoquinone.[8]

Linewidth variations can also occur in the e.s.r. spectrum as a result of restricted rotation, again provided that the rate of rotation is compatible with the timescale of the e.s.r. experiment. An example of restricted rotation can be found in the terephthalaldehyde radical anion where, at room temperature, the spectra of both the *cis*- and *trans*-isomers are observable.[9]

The 2-pivaloyl-1,4-benzoquinone radical anion therefore presents an intriguing problem as, if prepared by alkali-metal reduction, both cation migration (albeit between two non-equivalent sites) and restricted rotation (of the pivaloyl group) are possible. We have therefore undertaken a study of the e.s.r. spectrum of this radical anion, in tetrahydrofuran, with Li^+, Na^+, or K^+ as the counter-ion, to establish whether or not linewidth variation is observed, and, if it is observed, to try to establish whether the variation is due to cation migration or restricted rotation. As a preliminary to these investigations we have examined the radical anion prepared by electrochemical reduction in dimethylformamide.

Experimental

All vacuum operations were undertaken using standard high-vacuum techniques.

Materials.—Tetrahydrofuran (BDH) was purified as described previously[10] and stored over sodium–potassium alloy until required. Dimethylformamide (Lancaster Synthesis) was distilled under reduced pressure and stored over a 4 Å molecular sieve until required. 2-Pivaloyl-1,4-benzoquinone was prepared by oxidation of 2′,5′-dihydroxypivalophenone with silver(I) oxide.[11] Repeated recrystallisation from light petroleum (b.p 60—80 °C) gave bright yellow crystals, m.p. 348—349 K (lit.,[11] 348—348.5 K). The compound's structure was substantiated by ^1H n.m.r. in $CDCl_3$ at 60 MHz. Lithium, sodium, and potassium were all washed with light petroleum before use.

Procedure.—The concentrations of the solutions of the parent compound, for electrochemical reduction, were in the range $2—4 \times 10^{-3}$M, with tetrabutylammonium iodide (BDH) as the supporting electrolyte (0.1 mol l^{-1}).[12]

Solutions of 2-pivaloyl-1,4-benzoquinone in tetrahydrofuran were prepared by the standard methods described previously.[10] The concentration of the quinone was in the range $2—3 \times 10^{-3}$ mol l^{-1} and the radical anion was prepared from these solutions, by alkali-metal reduction, as described.[10] Metal films were used in the experiments involving sodium and potassium and small pieces of metal in experiments involving lithium.

Spectroscopic Measurements.—All e.s.r. spectra were recorded on a Varian E3 spectrometer, the magnetic field sweep of which was calibrated with Fremy's salt.[13] The temperature of the samples was controlled by means of a Varian E4557 variable-temperature unit.

Computer Simulation of E.S.R. Spectra.—Computer simulations of e.s.r. spectra were obtained using a Data General Nova computer on-line to the spectrometer or on a VAX 11/785 computer linked to a Calcomp plotter. The program used in the simulation of spectra exhibiting linewidth variation employed the modified Bloch equations appropriate to a two-jump process in which two sets of three non-equivalent protons interchange their splitting constants. The program allowed for the possibility of adding further non-modulating nuclei. The hyperfine splitting constants quoted from these simulations are considered to be accurate to ± 2 μT. Spectra not exhibiting linewidth variation were simulated using a constant linewidth program. The hyperfine splitting constants obtained from these simulations are considered to be accurate to ± 1 μT.

Molecular-orbital Calculations.—Molecular-orbital calculations were undertaken using a VAX 11/785 computer. The influence of an alkali-metal counter-ion upon the spin distribution was simulated by applying a perturbation to the value of α_0 for the oxygen atom adjacent to the counter-ion. Rotation of the pivaloyl group was simulated by variation of the appropriate β_{CC}.

Results and Discussion

Electrochemical Reduction in Dimethylformamide.—Electrochemical reduction of 2-pivaloyl-1,4-benzoquinone in dimethyl-

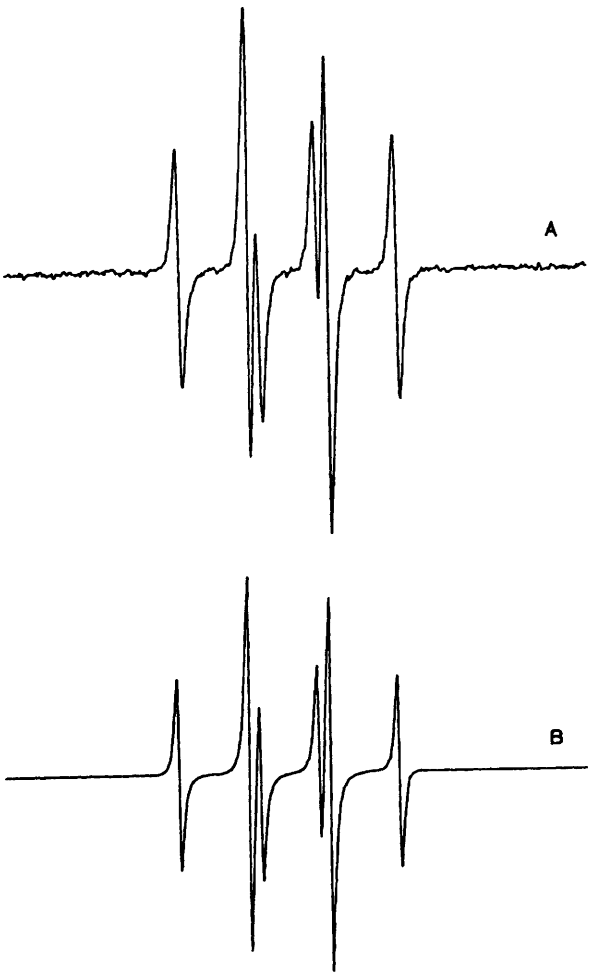


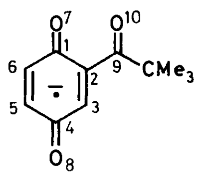
Figure 1. The experimental e.s.r. spectrum of the 2-pivaloyl-1,4-benzoquinone radical anion, in dimethylformamide, at 242 K (A) together with its computer simulation (B) (parameters as given in the text)

Table 1. Possible combinations of experimental hyperfine splitting constants (in μT) for the 2-pivaloyl-1,4-benzoquinone radical anion, with K^+ as the counter-ion, in tetrahydrofuran

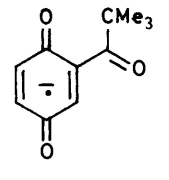
	Average		Average		Average
272 + 315	294	263 + 172	218	180 + 270	225
272 + 172	222	263 + 315	289	180 + 270	225

formamide gives an e.s.r. spectrum (illustrated in Figure 1) which is readily interpreted in terms of a single species with three doublet proton hyperfine splittings, two of which appear to be accidentally equivalent (or nearly so). Virtually identical spectra were recorded over the temperature range 236—326 K, that at 242 K having a(H) 270, 228, and 228 μT.

Two conformers, **A** and **B**, are possible for the 2-pivaloyl-1,4-benzoquinone radical anion. It is possible that one of these is considerably more stable than the other, so that only a single species is observed. Alternatively, both conformers may be present but interconverting rapidly on the e.s.r. timescale so that the splitting constants observed are the 'averaged' values of the individual conformers. A McLachlan calculation[14] assuming rapid interconversion (with $\alpha_O = \alpha_C + 1.4\beta_{CC}$, $\beta_{CO} = 1.7\beta_{CC}$, $\beta_{C(2)C(9)} = 0.5\beta_{CC}$, and $\alpha_{Bu^t} = \alpha_C - 0.5\beta_{CC}$) gives predicted ($\lambda$ = 1.2 and Q = 2.2 mT) values for a(3-H), a(5-H), and a(6-H) of 308, 222, and 245 μT, respectively, but provides little help in the assignment of the experimental splitting constants.



A



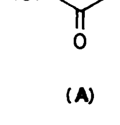
B

Alkali-metal Reduction in Tetrahydrofuran.—2-Pivaloyl-1,4-benzoquinone is readily reduced by potassium, sodium, and lithium to give a characteristic yellow–green solution of the radical anion.

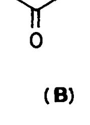
Potassium. At the low end of the temperature range over which spectra were recorded (163—336 K) two separate species were present in an approximate ratio of 1:1.5. The spectrum of each species was readily interpreted in terms of three non-equivalent hyperfine couplings (the predominant species has a(H) 272, 263, and 180 μT, the other species has a(H) 315, 270, and 172 μT. At temperatures above 315 K only a single species was observed with hyperfine parameters a(H) 303, 219, and 219 μT, similar to those obtained following electrochemical reduction. At intermediate temperatures the spectra exhibit linewidth variation.

It is clear that the two species identified at lower temperatures rapidly interconvert at 315 K and, consequently, that their hyperfine splitting constants have to be paired with one another as required to obtain this latter spectrum. There are, in fact, two sets of pairings which give hyperfine parameters consistent with the spectrum observed at 315 K; these are summarised in Table 1. Although both sets of pairings could lead to apparently similar 'averaged' spectra, the computer simulation of these spectra over the complete temperature range indicates that the first set in Table 1 is correct. The second set fails to give the correct line positions required by the experimental spectra. We therefore conclude that the 272 μT splitting interchanges with the 315 μT splitting, and likewise that the 263 μT splitting interchanges with the 172 μT splitting and that the 180 μT and 270 μT splittings interchange.

We first investigated the possibility that the two species were conformers (**A**) and (**B**). Huckel calculations, with the McLachlan modification, were therefore undertaken to test this possibility. Conformer (**A**) was represented in the calculations by decreasing h_O for O(7) and O(10) from 1.4 to 1.0 to allow for the interaction between adjacent carbonyl oxygen atoms. Conformer (**B**) was represented by the inclusion of an auxiliary inductive parameter of −0.25 at C(3) to allow for the interaction between the oxygen of the carbonyl group and the proton at this position. In both calculations $\beta_{C(2)C(9)}$ was taken to be $0.9\beta_{CC}$. The hyperfine splitting constants (in μT) predicted for these two conformers (λ = 1.2 and Q = 2.2 mT) are illustrated below:



(A)



(B)

Table 2. Hyperfine splitting constants (in μT) and values of τ for the 2-pivaloyl-1,4-benzoquinone radical anion, with K^+ as the counter-ion, in tetrahydrofuran. The values presented are taken from best-fit computer simulations of the experimental spectra

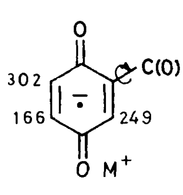
	Species (i)				Species (ii)			
T/K	a(3-H)	a(5-H)	a(6-H)	$10^8\,\tau$/s	a(3-H)	a(5-H)	a(6-H)	$10^8\,\tau$/s
185	272	180	263	120	315	270	172	80
203	272	180	263	60	315	270	172	40
215	272	180	263	30	315	270	172	20
225	272	180	263	22	315	270	172	15
230	272	180	263	15	315	270	172	10
240	272	180	263	10.5	315	270	172	7
253	272	180	263	5	315	270	172	3.5
265	275	177	262	4.3	319	267	171	2.9
277	279	175	262	3	323	265	171	2.1
287	281	175	262	2.1	325	265	171	1.5

Table 3. Activation parameters for intramolecular cation migration in the 2-pivaloyl-1,4-benzoquinone radical anion, with K^+ as the counter-ion, in tetrahydrofuran at 238 K

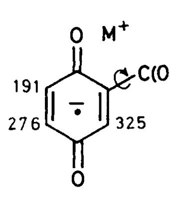
	$10^8\,\tau$/s	$\Delta G^{\ddagger}$/ kJ mol^{-1}	E_a/ kJ mol^{-1}	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J mol^{-1} K^{-1}
Species (i)	10.7	26.1	18.1	16.2	−41.7
Species (ii)	7.3	25.3	17.9	15.9	−39.6

It is apparent that these predicted splitting constants do not satisfactorily reproduce the experimental values. The parameters used in the calculations are those which have proved successful for similar systems in the past.[8] Furthermore, small variations either side of the quoted values do not result in a significant improvement in the agreement. A more serious problem, however, is that the calculated splitting constants do not invert upon interchange in the same way as the experimental values where, in particular, 263 μT interchanges with the 172 μT whilst 180 μT interchanges with 270 μT.

We therefore investigated the second possibility that the two conformers do not result from restricted rotation of the pivaloyl group but from a cation-migration process. A second series of calculations was therefore undertaken assuming rapid rotation of the pivaloyl group and simulating the presence of the alkali-metal counter-ion adjacent to a particular carbonyl group by modifying the appropriate h_O value. The value of $h_O = 1.70$ was selected to represent the influence of the K^+ ion.[8] The predicted hyperfine splitting constants are illustrated below:



(i)



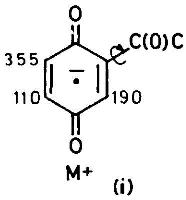
(ii)

Not only do these values agree remarkably well with the experimental values for the two species (see Table 2) they also average correctly. In addition the predicted values 175 and 262 μT interchange with inversion to 265 and 171 μT in accord with the experimental observations.

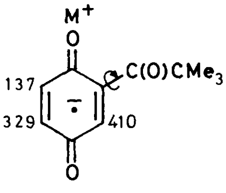
We therefore conclude that the experimental hyperfine splitting constants should be assigned as illustrated immediately above and that the two species observed result from two alternative cation locations rather than from two rotational conformers.

Sodium. It is apparent that the spectra observed when Na^+ is the counter-ion result from a mixture of two species, one with Na^+ hyperfine coupling and one without. The species without Na^+ hyperfine coupling also appears to exhibit linewidth variation and the complexity of these spectra is such that their interpretation adds little further information to our assignments at this stage.

Lithium. Spectra were recorded in the range 233—344 K and can be interpreted as comprising a mixture of two species over the whole of this temperature range (see Table 4). The species predominating at 233 K has hyperfine splitting constants (188, 123, and 319 μT) close to those anticipated for ion-pair species (i) in the presence of Li^+. An h_O value of 2.05, to allow for the interaction of the Li^+ ion with the appropriate carbonyl oxygen atom (see below), has been used in other calculations.[8] In contrast, the second species present in this system, which predominates at 344 K, has hyperfine splittings which vary with temperature to a far greater extent than any of the other species so far described. At low and intermediate temperatures the splittings are similar to those anticipated for the appropriate ion-pair species (ii) with free rotation of the pivaloyl group (see below).



(i)



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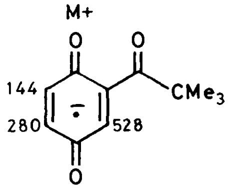
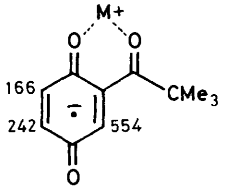


(iii)



(iv)

At the high end of the temperature range, however, the splittings are very different to those in the other systems described so far; in particular the comparatively large value of 550 μT. We have therefore considered the possibility that, at the higher end of the temperature range, the stronger interaction expected with the Li^+ counter-ion results in a 'locking' of the pivaloyl group. A calculation based on interaction with O(7) only ($h_O = 2.05$) gives the predicted splittings as for species (iii) above. These are close to the experimental splittings at 344 K (see Table 3) but are improved further if interaction involving both O(7) and O(10) is assumed [species (iv), $h_O = 1.90$].

This latter ion-pair arrangement would also explain the very significant da/dT values for this species as its nature slowly changes from species (ii) to species (iv) over the temperature range.

Linewidth Variation with K^+ *as the Counter-ion.*—As detailed above, e.s.r. spectra recorded at 163 K comprise the spectra of two separate species assigned to ion pairs with the K^+ ion adjacent to the carbonyl oxygen atoms, but with the pivaloyl group freely rotating. As the temperature is raised linewidth variation is observed until at 336 K the spectrum becomes that of a single species with splitting constants appropriate to the

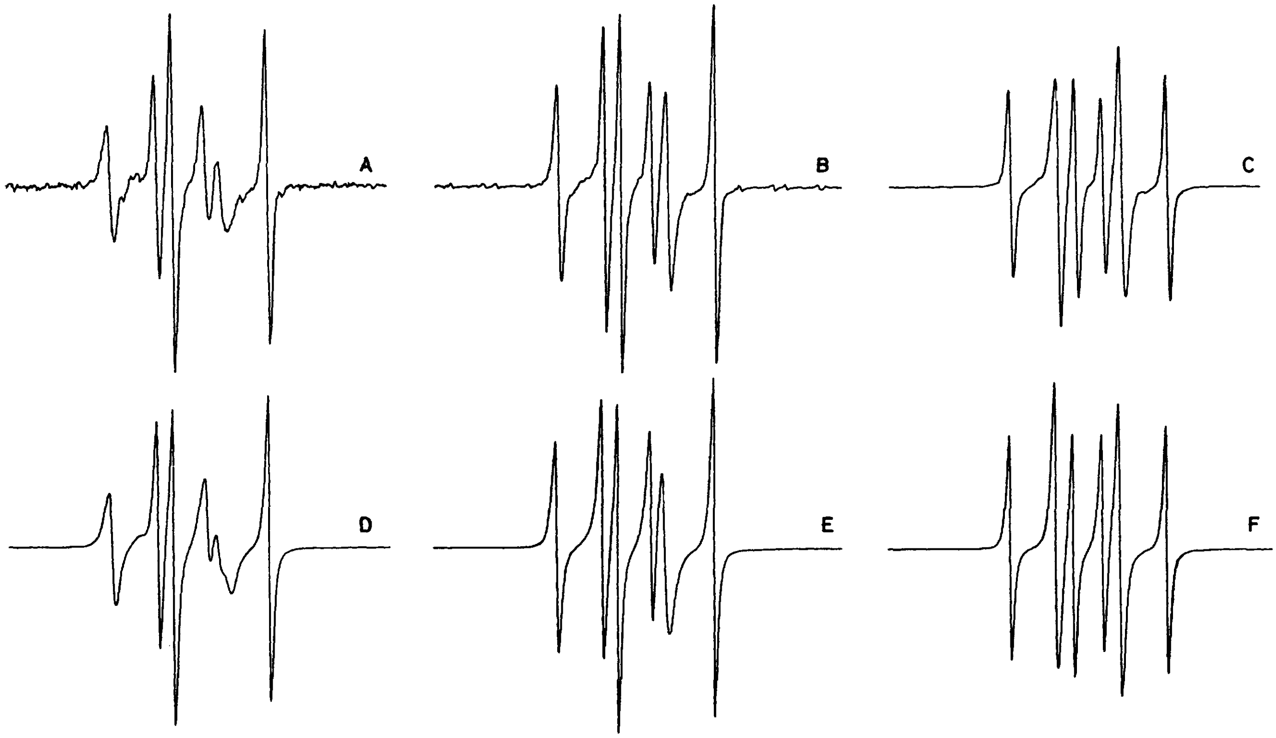


Figure 2. The experimental e.s.r. spectra of the 2-pivaloyl-1,4-benzoquinone radical anion, in tetrahydrofuran, with K^+ as the counter-ion, at 225 (A), 240 (B), and 287 K (C), together with their computer simulations [(D), (E), and (F), respectively; parameters as given in Table 2]

'averaged' values for species (i) and (ii). Each spectrum obtained was simulated using the program described above, appropriate to a two-jump process in which two sets of three non-equivalent protons interchange their splitting constants. Representative experimental spectra (at 225, 240, and 287 K) together with their computer simulations are shown in Figure 2. The parameters used in these simulations are summarised in Table 2 and the activation parameters in Table 3.

As can be seen from Table 3 the activation energies for the cation migration from species (i) to species (ii) and for the reverse process are virtually identical, as are the values of $\Delta S^{\ddagger}$. Indeed, the observed activation energies (of *ca.* 18 kJ mol^{-1}) are close to the activation energies observed for the K^+ migration in benzoquinone, 2,5-dimethylbenzoquinone, and 2,3-dimethylbenzoquinone radical anions in 1,2-dimethoxyethane (14.2,[2] 13.4,[6] and 16.7[6] kJ mol^{-1}, respectively), showing that the nature and position of substituents exert only a minor influence. A negative $\Delta S^{\ddagger}$ value would be anticipated for a migration process such as this. In the initial state the electronegative oxygen of the carbonyl group can act as a solvating agent for the cation. There will therefore be an increase in the number of solvent molecules involved in solvating the cation in the transition state relative to the initial state.

Spectra Obtained with Na^+ *as the Counter-ion.*—The interpretation of these spectra is complicated by the presence of two separate types of species and, due to their poor resolution, a complete spectral interpretation and computer simulation was attempted for only one temperature (257 K). This interpretation shows that the spectrum of one species (species X) exhibits linewidth variation in a manner very similar to the system described immediately above. For this species one set of hyperfine splitting constants (280, 175, and 266 μT) lies close to those of species (i) and the other set (323, 265, and 175 μT) lies close to those of species (ii). The spectrum of the second species (species Y) is quite different both in the magnitude of its hyperfine splitting constants (357, 156, and 304 μT) and in the fact that it indicates hyperfine coupling to the ^{23}Na nucleus [$a(^{23}Na)$ 35 μT]. The latter species (Y) must, presumably, be a much closer ion pair than species X. The experimental splitting constants lie close to those that might be expected for a species such as (ii) with Na^+ as the counter-ion. Unfortunately, owing to the complexity of the experimental spectrum, it is not possible to detect, within the spectrum, a contribution from a species of type Y(i).

Equilibrium with Li^+ *as the Counter-ion.*—The experimental spectra obtained with Li^+ as the counter-ion consist of a mixture of those of species (i) and (ii)/(iv). Spectra were recorded over the temperature range 233—344 K and the best-fit parameters required to simulate these spectra are summarised in Table 4. A least-squares analysis of the corresponding log K *vs.* $1/T$ plot gives a ΔH° value for the equilibrium:

$$\text{species (i)} \rightleftharpoons \text{species (ii)/(iv)}$$

of 11.9 ± 0.5 kJ mol^{-1}. It is interesting to note that higher temperatures, which would be expected to favour a closer ion-pair arrangement, favour species (iv). Presumably this species is favoured because the interaction of the counter-ion with both O(7) and O(10) increases its stability.

The positive ΔS° (39.1 J mol^{-1} K^{-1}) for this equilibrium is consistent with the proposed nature of species (iv) in which the interaction of the Li^+ ion with both carbonyl oxygen atoms would be expected to release solvent molecules.

Temperature Dependence of the Hyperfine Splitting Constants.—The da/dT values obtained when either K^+ or Li^+ is

Table 4. Hyperfine splitting constants (in μT) and equilibrium proportions for the 2-pivaloyl-1,4-benzoquinone radical anion, with Li^+ as the counter-ion, in tetrahydrofuran. The values presented are taken from best-fit computer simulations of the experimental spectra

	Species (i)				Species (ii)/(iv)			
T/K	a(3-H)	a(5-H)	a(6-H)	%	a(3-H)	a(5-H)	a(6-H)	%
233	188	123	319	81	439	292	120	19
242	187	122	319	77	450	285	119	23
252	185	122	319	73	463	276	118	27
262	184	122	320	68	473	266	118	32
273	184	122	323	64	491	262	117	36
281	183	119	324	59	499	255	117	41
292	183	117	327	55	513	246	114	45
300	182	116	327	52	519	242	114	48
310	183	113	328	48	529	239	114	52
321	179	113	331	44	535	234	113	56
333	179	113	334	40	544	231	112	60
344	179	109	334	37	550	228	111	63

Table 5. Values of 10^2 (da/dT)/μT K^{-1}) for the lithium 2-pivaloyl-1,4-benzoquinone radical anion, with Li^+ or K^+ as counter-ion, in tetrahydrofuran

Counter-ion		da(3-H)/dT	da(5-H)/dT	da(6-H)/dT
Potassium	species (i)	8.8	4.9	−0.1
	species (ii)	9.8	−4.9	−0.1
Lithium	species (i)	−7.9	−12.7	15.0
	species (ii)/(iv)	103	−58.8	−8.0

the counter-ion are summarised in Table 5. The values when K^+ is the counter-ion are similar for both species (i) and (ii) indicating that both of these species must be 'loose' ion pairs, with the overall da/dT values dominated by changes in spin distribution with temperature rather than by changes in the degree of interaction of the radical anion with the counter-ion. In contrast the da/dT values when Li^+ is the counter-ion and adjacent to O(7) are large and more informative. These values, particularly those for the protons at positions 3 and 5, are much larger than might be expected for a change in degree of interaction of the counter-ion with the carbonyl oxygen as a function of temperature. Higher temperatures, favouring a closer ion pair, should result in a negative da/dT value at position 6 and positive da/dT values at positions 3 and 5. It therefore appears that the nature of this species changes over the temperature range with a species such as (ii) being favoured at the lower temperatures and a species such as (iv) being favoured at the higher temperatures. The predicted splitting constants for these two species are illustrated above. At position 3 the predicted splitting constant changes from species (ii) to (iv) from 410 to 554 μT which, together with the positive contribution expected on temperature grounds alone (owing to stronger ion-pair interaction), predicts a very large positive da(3-H)/dT. At position 5 the predicted change is from 329 to 242 μT. This large negative value would be counteracted to some extent by the positive contribution resulting from a temperature change which leads to a stronger ion-pair interaction. Finally at position 6 the predicted change is from 137 to 166 μT, counterbalanced by the negative contribution from the temperature effect. All of these predictions fit remarkably well with the observed trends.

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