Influence of Solvent and Cation on the Properties of Oxygen-containing Organic Anions. Part 2.[1] Radical Anions derived from 2,5-Diarylfurans

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The e.s.r. spectra of radical anions of 2,5-diarylfurans were studied in several polar aprotic solvents with the cations of Li, Na, K, Rb, and Cs as counter-ions. The electron spin densities obtained from the hydrogen coupling constants for the 3 and 4 ring positions of the 2,5-diphenylfuran radical anions and the electron spin densities of the *para*-positions of the phenyl groups were analysed by multiple linear regression. A triple linear correlation with Dimroth–Reichardt E_T^N and Gutmann DN parameters of the solvent and the cation radius r_M was found. Hückel–McLachlan electron spin density calculations to fit the experimental values were performed. The values of the Coulomb parameter δ_O for oxygen which had to be used in order to obtain the best fit show that the oxygen–metal distance controls the observed electron spin densities. One can conclude that this distance increases when the solvent has a higher ability for dipolar interaction with an ion pair (measured by E_T^N), a higher capacity for electron-pair donation (measured by DN), and the cation a higher capacity to accept electron pairs from the solvent (smaller radius r_M).

The influence of solvation of radical anions and ion pairs has been studied by means of e.s.r. spectroscopy, through the analysis of the variation in the observed hyperfine splitting constants (h.s.c.). This subject has been approached theoretically either by adjusting the parameters in spin density calculations,[2–5] or using the reaction field formalism (Kirkwood–Onsager and Block–Walker theories).[6,7] Other authors found correlations between the values of h.s.c. and some physical properties of the medium such as the dipole moment,[8,9] the dielectric constant,[9–11] the molar fraction of a cosolvent,[12–16] and some empirical solvent parameters such as Kosower's Z,[11,17–19] Reichardt's E_T^N[8,20,21] and Gutmann's AN parameter.[22]

The influence of the cation on the structure of the ion pairs has been studied in a similar way by searching for a correlation between the observed h.s.c. and some cation characteristics such as r_M^{-1} (r_M = ionic radius), $r_M^{-\frac{1}{2}}$[5,23–26] (both known to be proportional to the electron affinity), or r_M itself.[27]

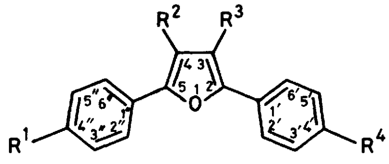
We report now on the influence of solvation and cation on the electron spin density distribution in the radical anions derived from 2,5-diphenylfuran by reduction with alkali metals in various polar aprotic solvents.

Recently a correlation was reported for the selectivity factor of the alkylation of acetophenone enolates as a function of the solvent parameters E_T^N,[28] DN,[29] and the ionic radius r_M of the cation.[1] E_T^N, for polar aprotic solvents, expresses the capacity for dipolar interaction of the solvent with a solute and DN the capacity for electron-pair donation of the solvent to a solute. A correlation including both solvent and cation characteristics has the advantage of allowing the analysis of a greater number of experimental data which increases the statistical significance of the correlations obtained and gives a better understanding of the phenomena involved.

We intended to apply the method described in Part 1[1] in order to try to find a correlation of the solvent and cation parameters with the variations observed for the spin density distribution in the radical anions derived from 2,5-diphenylfuran.

Results and Discussion

Cyclic voltammetry experiments for compounds (**1**)—(**4**) show a first reversible reduction wave with highly negative $E_{\frac{1}{2}}$ potentials between −2.48 and −2.39 V, showing the appearance of stable radical anions with an intact furan ring. For the reduction of (**1**) $E_{\frac{1}{2}}$ −2.435 V is obtained.



(**1**) $R^1 = R^2 = R^3 = R^4 = H$
(**2**) $R^1 = R^4 = CH_3, R^2 = R^3 = H$
(**3**) $R^1 = R^4 = H,\ R^2R^3 = CH_2CH{=}CHCH_2$
(**4**) $R^1 = R^4 = H, R^2 = R^3 = C_6H_5$

The reduction of the compounds (**1**)—(**3**) with alkali metals leads to particularly stable solutions of radical anions (many days, even at room temperature) with well resolved e.s.r. spectra as exemplified in Figure 1. The e.s.r. spectra of the radical anions obtained from (**4**) have a poorer resolution, due probably to the high number of small h.s.c.

The highly negative reduction potential of these compounds explains why (**1**) is not reduced by Li in less polar solvents such as diethyl ether (DE) and dioxane (DO). Table 1 lists the h.s.c. of the radical anions obtained by reduction of (**1**)—(**4**) with K in 1,2-dimethoxyethane (DME). These values were obtained by simulation of the corresponding e.s.r. spectra. The theoretical values calculated by Hückel–McLachlan method using as McConnell constants Q^H_{CH} −2.5 and $Q^H_{C\text{-}CH_3}$ +3.0 mT are also listed in Table 1. The parameters used are compatible with a nearly planar conformation of the radical anions.

The assignment of the h.s.c. to the 4′- and 4″-position results from the e.s.r. spectral simulation of the dimethylated derivative $(\mathbf{2})^{-\bullet}K^+$ (Figure 1). Identically, the e.s.r. spectrum simulation of $(\mathbf{3})^{-\bullet}K^+$ allows the assignment to positions 3 and 4 which are confirmed by the simulation of the e.s.r. spectrum of $(\mathbf{4})^{-\bullet}K^+$.

The signs of the h.s.c. referred to in Table 1 are based on spin-density calculations by the Hückel–McLachlan method and on triple-resonance experiments for the radical anion $(\mathbf{4})^{-\bullet}$.

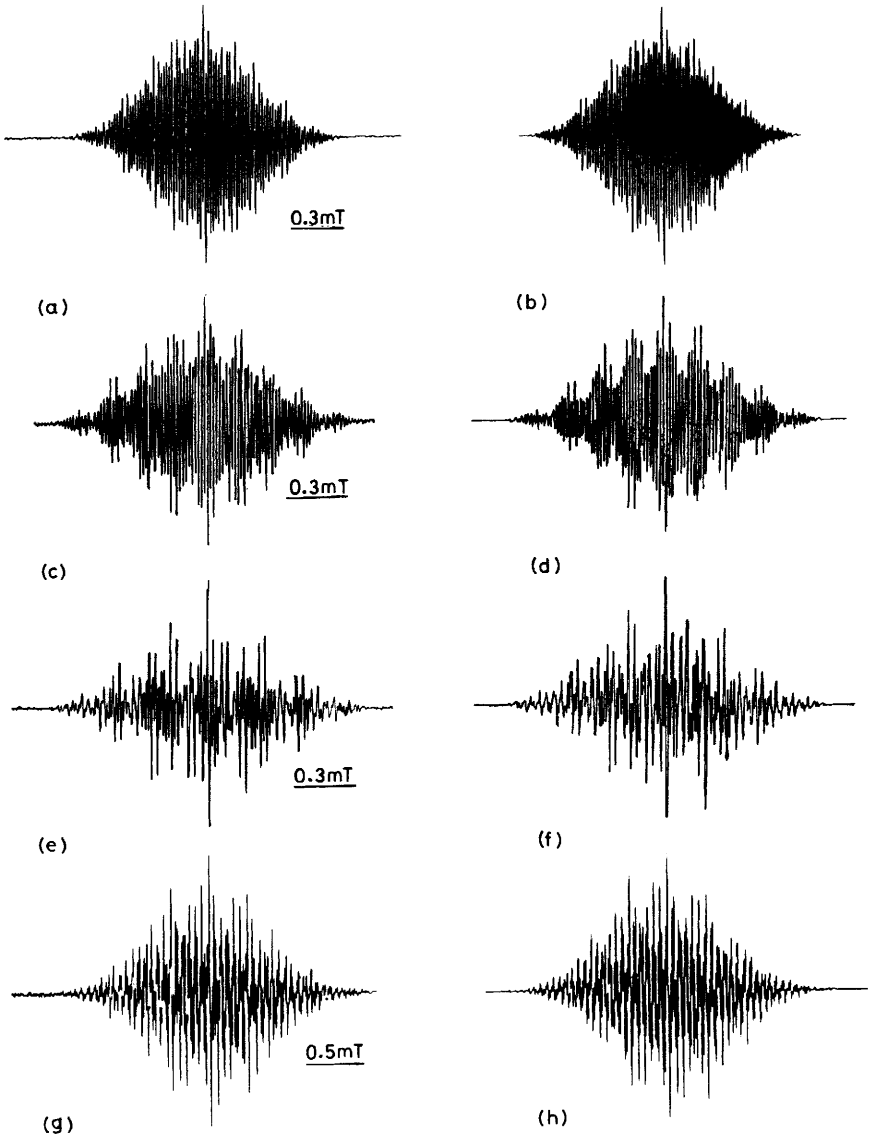


Figure 1. Experimental (left side) and simulated (right side) e.s.r. spectra of the radical anions: a, b: $(\mathbf{1})^{-\cdot}\mathrm{K}^+$ (DME); c, d: $(\mathbf{1})^{-\cdot}\mathrm{Li}^+$ (DME); e, f: $(\mathbf{1})^{-\cdot}\mathrm{K}^+$ (MTHF); g, h: $(\mathbf{2})^{-\cdot}\mathrm{K}^+$ (DME)

The non-equivalence of the two *ortho* positions and of the two *meta* positions in each phenyl ring is evidence for a rigid conformation of these groups in relation to the furan ring in the e.s.r. time scale, not allowing any free rotation. This restricted rotation was accounted for in the calculations by using a Coulomb-adjusting parameter δ_C -0.1 for C-2′ and -2″.

The spin distribution in the aromatic system is a function of the nature of the cation and of the solvent as shown in Figure 1 and in Table 2. In Table 2 spin-density values are shown for positions 3, 4, and 4′,4″ in the radical anions obtained by the reduction of (**1**) with different alkali metals and in different polar aprotic solvents. The spin-density values for the other positions are omitted since they are independent of the nature of the cation and of the solvent. They have the values shown in Table 1.

The h.s.c. due to the cation were not observed in the e.s.r. spectra of the radicals obtained by the reduction of (**1**) with Li, Na, and K, nor with Rb and Cs in dimethoxyethane (DME), but an h.s.c. is observed in tetrahydrofuran (THF) and methyltetrahydrofuran (MTHF) for Cs (a_{Cs} 0.088 mT in MTHF; a_{Cs} 0.062 mT in THF). The observed dependence on the cation and on the solvent shows that these radical ions exist, in solution, associated with the counter-ion and are therefore ion pairs.

The observed variations of the spin distribution in the aromatic system are interpreted theoretically by introducing into the spin-density calculations a variable parameter δ_O for the Coulomb integral of oxygen $\alpha_O = \alpha_C + \delta_O\ \beta_{CC}$, as shown in Figure 2. Spin densities for positions 3, 4, and 4′,4″ are more affected by the variation of δ_O than other positions. On increasing δ_O an increase in the h.s.c. of the 3- and 4-H protons and a decrease in the h.s.c. of the 4′- and 4″-H is expected.

According to McClelland[30] the Coulomb parameter δ_O for the oxygen atom is inversely proportional to the distance between anion and cation. Comparing the experimentally observed spin distribution variations with the theoretical variations upon changing the δ_O parameter, we conclude that these ion pairs are more separated by solvent with Li and in solvents with a higher solvating power for ions (smaller δ_O).

The expected influence of the cation and of the solvent on the interionic distance d is described by the relationships (1) and (2). According to the spin-density values shown in Table 2, an

Table 1. Calculated and experimental h.s.c. (mT) for radical anions derived from arylfurans (**1**)—(**4**) (counter-ion K, solvent DME). The h.s.c. were calculated by the McLachlan method. Q^{H}_{CH} −2.5, $Q^{H}_{C\text{-}CH_3}$ 3.0 mT

		H.s.c. (mT) Positions					
Compound		3,4	2′,2″	3′,3″	4′,4″	5′,5″	6′,6″
(**1**)	Calc.[a]	−0.080	−0.176	0.041	−0.325	0.070	−0.223
	Exp.	−0.080	−0.200	0.040	−0.381	0.060	−0.241
(**2**)	Calc.[b]	−0.080	−0.180	0.039	0.387 (6 H)	0.075	−0.229
	Exp.	−0.077	−0.204	0.045	0.401 (6 H)	0.066	−0.256
(**3**)	Calc.[c]	0.105	−0.171	0.040	−0.326	0.070	−0.214
	Exp.	0.110	−0.200	0.034	−0.381	0.060	−0.247
(**4**)	Calc.[d]	0.029 (2‴, 2⁗) 0.034 (6‴, 6⁗) 0.056 (4‴, 4⁗) 0.012 (3‴, 3⁗) 0.014 (5‴, 5⁗)	−0.179	0.048	−0.283	0.061	−0.200
	Exp.	0.027 (2‴, 2⁗) 0.039 (6‴, 6⁗) 0.057 (4‴, 4⁗) 0.007 (3‴, 3⁗) 0.007 (5‴, 5⁗)	−0.192	0.039	−0.345	0.057	−0.228

[a] δ_O 1.9; $\gamma_{12} = \gamma_{15} = 0.9$; $\gamma_{23} = \gamma_{34} = \gamma_{4.5} = 1.1$; $\delta_{C(2)} = \delta_{C(5)} = -0.05$; $\delta_{C(2')} = \delta_{C(2'')} = -0.1$. [b] Parameters as in *a* and $\delta_{C(4')} = \delta_{C(4'')} = -0.05$. [c] Parameters as in *a* and $\delta_{C(3')} = \delta_{C(3'')} = -0.05$. [d] Parameters as in *a* and $\delta_{C2'''),(2'''')} = 0.1$; $\delta_{C(6'),(6''),(6'''),(6'''')}$ −0.04.

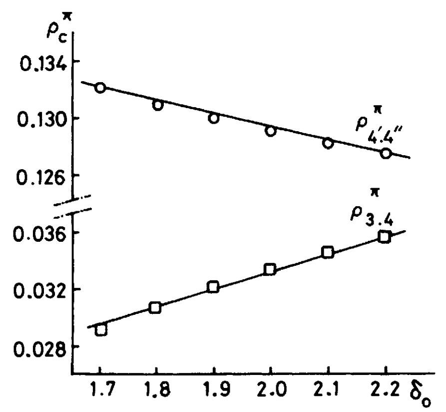


Figure 2. Calculated spin densities for 3,4, and 4′,4″ positions of $(\mathbf{1})^{-\bullet}$ as a function of the oxygen Coulomb parameter δ_O

$$\mathrm{Li > Na > K > Rb > Cs} \tag{1}$$

$$\mathrm{HMPA > DME > THF > MTHF > DO > DE} \tag{2}$$

apparently free radical anion is obtained by the reduction of (**1**) with K in hexamethylphosphotriamide (HMPA).

A correlation analysis with the two series of parameters used in the study of acetophenone enolates[1] allowed us to select the same parameters E^{N}_{T} and DN as being the ones which led to the most significant correlation by far in each series.

The correlation analysis of the experimental results in Table 2 by multiparametric linear regression analysis leads to expression (3) with the regression coefficients shown in Table 3.*

$$\rho^{\pi} = \rho^{\pi}_{0} + a E^{N}_{T} + b\,\mathrm{DN} + c\, r_{M} \tag{3}$$

In order to determine the relative importance of the solvent parameters (E^{N}_{T} and DN) and the ionic radius r_M of the cation, the partial regression coefficients *a′*—*c′* defined in the statistics of multiple linear regression[31] were calculated. The contribution of the different parameters are given as percentages by expression (4). Table 3 contains the number of experimental

$$\bar{x} = 100\, x'/a' + b' + c' \qquad x = a, b, c \tag{4}$$

points (*n*), the correlation coefficient (*R*), the standard deviation (σ), the Fisher parameter (*F*),[31] and the contribution of the different parameters as percentage ($\bar{a}$, $\bar{b}$, $\bar{c}$). The fact that $\bar{a} \gg \bar{b}$ means that the variations of the non-specific solvation effects (dipolar interactions) described by the variation of E^{N}_{T} are more important in the solvation of the ion pair $(\mathbf{1})^{-\bullet}\mathrm{M}^{+}$ than the variation of the capability of the solvent to produce the specific cation solvation effects (electron pair donation) described by DN. The variations of specific anion solvation are irrelevant because we are dealing with aprotic solvents.

According to Figure 2, spin density $\rho^{\pi}_{4',4''}$ increases and $\rho^{\pi}_{3,4}$ decreases when ion pair solvation becomes stronger (smaller δ_O and larger interionic distance *d*) which is consistent with the signs of *a*—*c* shown in Table 3 for the two correlations. The fact that the sign of *c* is opposite to that of *a* and *b* shows that this system behaves more like an ion pair of an aromatic hydrocarbon radical anion than like an ion pair derived from other oxygen-containing compounds such as aromatic ketones. The more concentrated the positive charge the more the dipolar interactions and electron-pair donation pull away the cation from the anion. This result is consistent with the excessive charge densities for the radical anion calculated by the HMO method which shows that all the negative charge is delocalized on carbon atoms while on the oxygen atom there is a partial positive charge.

We conclude that it is the distance *d* between the radical anion and the counter-ion that controls the experimentally observed variation in spin distribution. The same conclusion had been reached by studying the regioselectivity of the methylation acetophenone enolate in polar aprotic solvents.[1]

Experimental

Materials.—Compounds (**1**)—(**4**) were synthesized and purified as described elsewhere.[32–34]

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* *Note added in proof:* In this case, contrary to what was found in Part 1, there is no improvement if r_M^{-3} is used instead of r_M.

Table 2. Experimental spin densities ($\rho^{\pi}_{3,4}$ and $\rho^{\pi}_{4',4''}$) for $(\mathbf{1})^{-\bullet}M^{+}$ in different polar aprotic solvents

Solvent[a]	Cation	$10^2 \times \rho^{\pi}_{3,4}$	$10^2 \times \rho^{\pi}_{4',4''}$	Solvent	Cation	$10^2 \times \rho^{\pi}_{3,4}$	$10^2 \times \rho^{\pi}_{4',4''}$
MTHF	Li	3.34	15.10	DO	K	3.91	14.92
THF	Li	3.10	15.28	MTHF	K	3.82	14.96
DME	Li	3.04	15.33	THF	K	3.45	15.12
DE	Na	3.82	15.01	DME	K	3.20	15.24
DO	Na	3.74	15.08	HMPA	K	2.95	15.48
MTHF	Na	3.47	15.11	DME	Rb	3.29	15.18
THF	Na	3.18	15.20	MTHF	Cs	4.19	14.86
DME	Na	3.08	15.30	THF	Cs	3.74	14.98
DE	K	4.01	14.84	DME	Cs	3.36	15.08

[a] For the meaning of solvent symbols see Experimental section.

Table 3. Results of triparametric linear regression analyses of ρ^{π}_{C} *versus* E^{N}_{T}, DN, and r_M: $\rho^{\pi}_{C} = \rho^{\pi}_{0} + a\,E^{N}_{T} + b\,DN + c\,r_M$, for ion pairs $(\mathbf{1})^{-\bullet}$

	ρ^{π}_{0}	a	b	c	n[a]	R[b]	σ[c]	F[d]	$\bar{a}$	$\bar{b}$	$\bar{c}$
$\rho^{\pi}_{3,4}$	4.056	−6.554	−0.004	0.670	18	0.939	0.0014	34.8	57.4	3.6	39.0
$\rho^{\pi}_{4',4''}$	18.814	+2.607	+0.007	−0.311	18	0.979	0.0004	106.5	47.4	14.9	37.7

[a] Number of experimental points n. [b] Multiple correlation coefficient R. [c] Standard deviation σ. [d] Fisher parameter F.

2-Methyltetrahydrofuran (MTHF), tetrahydrofuran (THF), dimethoxyethane (DME), diethyl ether (DE), dioxane (DO), hexamethylphosphotriamide (HMPA), and *NN*-dimethylformamide (DMF) were dried by known techniques.[1] Tetrabutylammonium perchlorate (B.D.H.) was dried *in vacuo* at 100 °C using P_2O_5 as drying agent.

Procedure.—The solutions of the radical anions were prepared by reduction of compounds (**1**)—(**4**) with different alkali metals (Li, Na, K, Rb, and Cs) in various polar aprotic solvents by known techniques.

E.s.r. spectra were recorded at room temperature using a Bruker ER 200D spectrometer. ENDOR and TRIPLE resonance spectra of the radical anion of compound (**4**) were recorded on a Varian E 109 spectrometer interfaced with a Bruker ENDOR–TRIPLE resonance system by courtesy of Drs. J. C. Evans and C. C. Rowlands, University College, Cardiff. The e.s.r. spectra were simulated[35] on a computer until the match with the experimental spectrum could not be further improved.

Cyclic voltammetry experiments were performed on a Princeton Applied Research potentiostat–galvanostat model 173, at room temperature using 10^{-3}M solutions of compounds (**1**)—(**4**) in DMF. Tetrabutylammonium perchlorate (0.1M) was used as a support electrolyte, the working electrode was a mercury drop electrode, and the reference was a saturated calomel electrode.

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