Influence of Solvent and Cation on the Properties of Oxygen-containing Organic Anions. Part 3.[†] Electron Spin Density on Alkali-metal Cations chelated by Radical Anions as a Function of Interionic Distance

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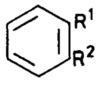
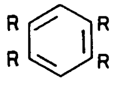
E.s.r. spectra of radicals derived by addition of several alkali-metals to 1,2-bispentamethylbenzoyl-, 1,2-dimesitoyl-, 1-benzoyl-2-mesitoyl-, and 1,2,4,5-tetramesitoyl-benzene were studied in nine aprotic solvents. The electron spin densities at the alkali-metal obtained from the experimental alkali-metal couplings together with previously published values (12 solvents combined with Li, Na, K, Rb, and Cs) correlate linearly with the empirical solvent parameters $E_T^N(30)$ and DN, and with the radius of the alkali cation. This is interpreted as a consequence of the interionic distance being controlled by dipolarity and Lewis basicity of the solvent, along with the cation radius.

The chelate ion pairs of alkali ions and radical anions of some 1,2-diaroylbenzenes[1–3] (**1**)—(**3**) and 1,2,4,5-tetramesitoylbenzene[4] (**4**) remain unique examples insofar as they show unusually large isotropic alkali-metal hyperfine splitting constants (h.s.c) in their e.s.r. spectra in solution. The sign of the metal hyperfine splitting constant (h.s.c.) a_M was determined either by ENDOR[5,6] or by e.s.r. linewidth analysis[7] and found to be positive. This shows that the electron spin density ρ_M at the alkali-metal is mainly a consequence of the strong overlap between the *ns* valence shell of the alkali-metal and the antibonding antisymmetrical π orbital of the unpaired electron.



(**1**) $R^1 = R^2 = 2,4,6\text{-}Me_3C_6H_2CO$
(**2**) $R^1 = PhCO$, $R^2 = 2,4,6\text{-}Me_3C_6H_2CO$
(**3**) $R^1 = R^2 = Me_5C_6CO$



(**4**) $R = 2,4,6\text{-}Me_3C_6H_2CO$

The theoretical calculations of the alkali-metal spin densities ρ_M for the radical anions of 1,2-dimesitoylbenzene ($\mathbf{1}^{\cdot -}$) with lithium, sodium, and potassium counter-ions[7] are consistent with the structure initially proposed by Herold *et al.*[3] for these ion pairs.

Both the knowledge of the structure of the ion pairs and the solvent dependency of the alkali-metal h.s.c.[4] make them very interesting models for the study of solvation effects allowing a more detailed understanding of their behaviour.

The calculations mentioned above yielded for each pair of a certain 1,2-diaroylbenzene radical anion and an alkali-metal cation a plot of the electron spin density ρ_M at the metal represented as a function of the oxygen–metal distance r_{OM}.[7] Hence by determining experimentally a_M in a certain solvent, and since $\rho_M = a_M/a_{M^0}$ (a_{M^0} being the atomic hyperfine splitting constant of the particular alkali-metal vapour), one is able to estimate r_{OM}.

The last two decades have seen a proliferation of solvent parameters and attempts to interpret solvent effects on reactivity and spectroscopic properties through single or multiple regression. Fairly good correlations are sometimes observed between h.s.c. and some solvent parameter, namely dielectric constant ε,[8,9] dipole moment μ,[10] Kosower's *Z* value,[9,11–13] Dimroth–Reichardt's E_T^N parameter,[10,14,15] and Gutmann's acceptor number AN.[16] In other cases, such correlations are clearly too poor. It may be that, in many such cases, a multiparameter regression analysis with two or more independent and complementary parameters fits quite well the solvent-dependent experimental data, by analogy with the Koppel–Palm treatment.[17]

In this study we intend to describe simultaneously the solvent and cation effect on the electron spin density ρ_M at the metal in ion pairs derived from 1,2-diaroylbenzenes (**1**)—(**3**) and 1,2,4,5-tetramesitoylbenzene (**4**). By doing so we are studying indirectly the effect of the solvent and the cation on the oxygen–metal distance r_{OM} since it can be estimated from ρ_M. In order to introduce into the correlation a parameter which is characteristic of the cation we used the ionic radius r_M. The choice of the solvent parameters included in the correlation is made through a preliminary single correlation analysis with the main solvent parameters referred in the literature, describing either the acidity and polarity of the solvent or their basicity. In this series of parameters the one that gives the more significant correlation is selected.

Results and Discussion

The experimental value of the alkali-metal h.s.c. and the spin densities of the alkali-metal ρ_M obtained from them, for the ion pairs derived from 1-benzoyl-2-mesitoylbenzene (**2**), 1,2-bispentamethylbenzoylbenzene (**3**), and 1,2,4,5-tetramesitoylbenzene (**4**), in several polar aprotic solvents, are shown in Table 1. We have omitted in the Table all the values already cited in the literature, namely those referring to 1,2-dimesitoylbenzene (**1**).[1,2,4,7] The spin densities have been calculated by ratio a_M/a_{M^0}.

[†] Part 2, M. L. T. M. B. Franco, M. C. R. L. R. Lazana, and B. J. Herold, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1407.

Table 1. Experimental alkali-metal h.s.c. and spin densities not yet referred in the literature for the ion pairs (**2**)—(**4**) in different polar aprotic solvents

Compound	Solvent[a]	Cation	H.s.c. (mT)	$10^2 \rho_M$
(**2**)	MTHF	Li	0.474	3.30
(**2**)	MTHF	Na	0.764	2.42
(**2**)	MTHF	K	0.148	1.80
(**2**)	DME	Na	0.708	2.24
(**2**)	DG	Na	0.685	2.17
(**2**)	DG	K	0.100	1.20
(**3**)	MTHF	Li	0.336	2.34
(**3**)	MTHF	Na	0.703	2.23
(**3**)	MTHF	K	0.149	1.81
(**3**)	DME	Li	0.377	2.60
(**3**)	DME	Na	0.688	2.18
(**3**)	DME	K	0.135	1.64
(**3**)	DME	Cs	1.027	1.25
(**3**)	DG	Na	0.667	2.11
(**3**)	DG	K	0.134	1.63
(**3**)	DMF	Na	0.590	1.87
(**4**)	DE	Na	0.521	1.65
(**4**)	DO	Na	0.442	1.40
(**4**)	DME	Na	0.392	1.24
(**4**)	DME	K	0.075	0.91
(**4**)	DG	Na	0.367	1.16
(**4**)	DG	K	0.072	0.87
(**4**)	DG	Cs	0.505	0.62
(**4**)	TG	Li	0.145	1.01
(**4**)	TG	Cs	0.485	0.59
(**4**)	DMF	Na	0	0
(**4**)	DMF	Cs	0	0
(**4**)	HMPA	Na	0	0

[a] For solvent symbols see Experimental section.

Table 2. Parameters of regression analysis leading to correlations for $\rho_M = \rho_M{}^0 + aX$, for the ion pairs $(\mathbf{1}^{\cdot-})$ Na$^+$ in different polar aprotic solvents

X	$10^2 \rho_M{}^0$	$10^2 a\ (t_a)$[a]	n[b]	r[c]	σ[d]	F[e]
DN	3.590	−0.058 (3.37)	11	0.747	0.289	11.39
$\Delta\nu_D$	3.509	−0.014 (1.32)	8	0.473	0.357	1.73
B_{KT}	3.484	−1.921 (1.09)	5	0.531	0.448	1.18
β	3.150	−1.465 (0.859)	6	0.394	0.435	0.737
Z	2.343	−0.001 (0.037)	8	0.015	0.349	0.001
AN	2.970	−0.072 (3.77)	6	0.884	0.167	14.23
E_T^N	3.054	−3.423 (4.28)	9	0.851	0.202	18.35
π^*	3.296	−1.733 (6.80)	6	0.959	0.134	46.21

[a] t Values. [b] Number of experimental points. [c] Correlation coefficient. [d] Standard deviation. [e] Fisher parameter.

In order to analyse the solvent dependency of ρ_M by one-parameter regression analysis, we have chosen the ion pairs $(\mathbf{1}^{\cdot-})$Na$^+$ because there are more experimental data available[1,2,4,7] and have tried the correlations with some empirical solvent parameters used in the literature to describe either polarity and Lewis acidity (E_T^N,[18] Z,[19] AN,[20] π^*[21]) or solvent basicity (DN,[20] $\Delta\nu_D$,[22] B_{KT},[23] β[21]). The results of this correlation analysis are summarized in Table 2 where the number of experimental data n, the correlation coefficient r, the standard deviation σ, and the Fisher parameter F are also included.

In the set of solvent basicity parameters, DN leads to the most significant correlation by far and was selected for multiple correlations. On the other hand, in the set of acidity parameters used, AN as much as E_T^N and π^* give fairly good correlations of comparable significance (see Table 2).

Our preference for E_T^N is based essentially on the circumstance that E_T^N has been determined and can be found in Tables[18] for a much higher number of solvents than π^*, allowing us to include more of our experimental data into the multiple regression analysis described below, which adds to the statistical significance of the correlations. It is also known that for those dipolar aprotic solvents known as Taft's select solvents a good linear correlation was found to exist between E_T^N and π^*. As our analysis is restricted to dipolar aprotic solvents, most of which belong to the category of Taft's select solvents, E_T^N and DN were selected. Multiparametric equations of the same form (1) already proposed in previous papers[24,25] for other magnitudes were thus used.

$$\rho_M = \rho_M{}^0 + aE_T^N + b\text{DN} + cr_M \qquad (1)$$

This correlation had been, however, established much earlier for the values of ρ_M published earlier[1,2,4] and the ones we are now reporting.[26] By trying to find out if this correlation was also applicable to other phenomena we found the correlations which will be published in Part 4,[27] as well as those which have already appeared.[24,25]

The results of the correlation analysis of the experimental data available for the ion paris of $(\mathbf{1}^{\cdot-})$—$(\mathbf{4}^{\cdot-})$ by applying the above equation are summarized in Table 3 which includes the number of experimental data n, the multiple correlation coefficient R, the standard deviation σ, the Fisher parameter F, and the t values of the different regression coefficients. The results in Table 3 show that the correlations based on the three explanatory variable equations (1) are highly significant (very high R and F values) but only the partial regression coefficients a and c are individually statistically significant for the ion pairs $(\mathbf{1}^{\cdot-})$M$^+$, $(\mathbf{3}^{\cdot-})$M$^+$, and $(\mathbf{4}^{\cdot-})$M$^+$ and only c is significant for $(\mathbf{2}^{\cdot-})$M$^+$ on the basis of the conventional t test.[28] Consequently b, or a and b, cannot be estimated with great accuracy as is shown by their large standard errors and this means that the explanatory variables E_T^N and DN are somewhat correlated in the set of experimental data used in this work. Although these parameters are usually regarded as linearly independent,[29,30] in the narrow range of solvents where the ion pairs derived from (**1**)—(**4**) may exist there is some collinearity as stated by the correlation coefficient R 0.809 (R 1 for perfect collinearity) observed in the set of experimental data corresponding to (**1**). This situation known as multicollinearity is not a serious problem when the correlations (1) are used for predictions because the higher R^2 the better the prediction, but may prevent the evaluation of the individual effects of the explanatory variables because it leads to large standard errors of the estimations.[28]

The substitution of DN in (1) for another parameter describing the electron pair donation capacity of the solvent, such as those referred in Table 3, leads to correlations where multicollinearity is even more severe, and compels some experimental data to be disregarded due to the lack of known values for these parameters for some solvents used, with the consequent reduction of statistical significance.

Table 3. Results of triparametric linear regression analysis of ρ_M *versus* E_T^N, DN, and r_M: $10^2\rho_M = \rho_M{}^0 + aE_T^N + b\text{DN} + cr_M$ for ion pairs derived from **(1)**—**(4)** with different alkali-metals in different polar aprotic solvents

Compound	$\rho_M{}^0$	$a\ (t_a)^a$	$b\ (t_b)^a$	$c\ (t_c)^a$	n^b	σ^c	R^d	F^e
(1)	4.344	−4.293	0.020	−1.613	29	0.117	0.981	212.35
		(6.07)	(1.55)	(23.16)				
(2)	6.637	−1.322	−0.070	−2.528	12	0.156	0.985	89.50
		(0.14)	(0.71)	(14.7)				
(3)	3.430	−1.991	−0.017	−1.262	16	0.093	0.977	83.11
		(2.61)	(1.21)	(15.76)				
(4)	2.775	−4.132	−0.003	−0.751	22	0.065	0.987	223.93
		(8.84)	(0.41)	(16.10)				

[a] *t* Values. [b] Number of experimental data. [c] Standard deviation. [d] Multiple correlation coefficient. [e] Fisher parameter.

Table 4. Results of linear regression analysis for correlations: $10^2\ \rho_M = \rho_M{}^0 + aE_T^N + cr_M$ for ion pairs derived from **(1)**—**(4)** with the different alkali-metals in different polar aprotic solvents

Compound	$\rho_M{}^0$	$a\ (t_a)^a$	$c\ (t_c)^a$	σ^b	n^c	R^d	F^e	$\bar{a}(\%)^f$	$\bar{c}(\%)^f$
(1)	4.584	−3.410	−1.607	0.120	29	0.979	301.22	26	74
		(7.95)	(22.52)						
(2)	6.533	−7.916	−2.483	0.152	12	0.985	141.77	20	80
		(3.91)	(16.00)						
(3)	3.632	−1.261	−1.254	0.096	16	0.974	119.78	27	73
		(2.66)	(15.45)						
(4)	3.223	−6.657	−0.662	0.154	22	0.920	52.22	57	43
		(8.12)	(6.18)						

[a] *t* Values. [b] Standard deviation. [c] Number of experimental data. [d] Multiple correlation coefficient. [e] Fisher parameter. [f] Percentage contribution of the parameters calculated through the partial regression coefficients.[17]

Table 5. Results of linear regression analysis for correlations: $10^2\ \rho_M = \rho_M{}^0 + b\text{DN} + cr_M$ for ion pairs derived from **(1)**—**(4)** with the different alkali-metals in different polar aprotic solvents

Compound	$\rho_M{}^0$	$b\ (t_a)^a$	$c\ (t_c)^a$	σ^b	n^c	R^d	F^e	$\bar{b}(\%)^f$	$\bar{c}^f$
(1)	4.796	−0.044	−1.614	0.180	29	0.952	126.26	19.1	80.9
		(3.68)	(15.03)						
(2)	6.644	−0.083	−2.537	0.147	12	0.985	150.65	19.5	80.5
		(4.10)	(16.90)						
(3)	3.595	−0.013	−1.233	0.113	16	0.963	83.90	8.6	91.4
		(1.18)	(12.94)						
(4)	3.240	−0.060	−0.771	0.129	22	0.944	78.26	42.3	57.7
		(10.08)	(8.53)						

[a] *t* Values. [b] Standard deviation. [c] Number of experimental data. [d] Multiple correlation coefficient. [e] Fisher parameter. [f] Percentage contribution of the parameters calculated through the partial regression coefficients.[17]

One way to remove multicollinearity is to drop one of the collinear variables, but in dropping DN from the model (1) we may be committing a specification error that arises from incorrect description of the solvent effect, that is not taking into account the specific solvation of the cation when dealing with ion pairs. The unspecified model is (2). The numerical results for

$$\rho_M = \rho_M{}^0 + aE_T^N + cr_M \qquad (2)$$

this correlation are shown in Table 4. All the partial regression coefficients are now statistically significant but the same occurs if one drops E_T^N from the model. In fact, dropping E_T^N leads to the still more incorrect model (3) where the polarity of the

$$\rho_M = \rho_M{}^0 + b\text{DN} + cr_M \qquad (3)$$

solvent is not taken into account. The numerical results for correlations (3) are shown in Table 5. One can see that when one of the variables E_T^N or DN is dropped, the solvent effect described by the missing parameter is absorbed by the remaining ones, leading to incorrect analysis of the solvent effect.

To overcome the problem of multicollinearity while keeping all the variables of model (1), the alternative estimation method, Principal Components Analysis,[28] can be carried out while retaining correlations (1) which are very good when applied in predictions.

The method lies in the transformation of the initial set of standardized explanatory variables* $(E_T^N)^s$, $(\text{DN})^s$, and $r_M{}^s$ into a new set of variables Z_i called principal components which are rigorously orthogonal and are linear correlations of the original ones [equation (4)].

$$Z_i = \alpha_i(E_T^N)^s + \beta_i(\text{DN})^s + \gamma_i r_M{}^s \qquad (4)$$

The maximum number of principal components is equal to the number of the initial explanatory variables. The first principal component absorbs and accounts for the maximum possible proportion of the total variations in the set of all the

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* A standardized variable is obtained by subtracting the average value of the variables from the value corresponding to each observation and dividing by the standard deviation of the observations.

Table 6. Principal components Z_i and parameters of regression analysis for correlations $\rho_M{}^s = \rho_M{}^0 + \alpha' Z_1 + \beta' Z_2 + \gamma' Z_3$

	$Z_1 = \alpha(E_T^N)^s + \beta(DN)^s + \gamma r^{s\,a}$			$Z_2 = \alpha(E_T^N)^s + \beta(DN)^s + \gamma r^{s\,a}$			$Z_3 = \alpha(E_T^N)^s + \beta(DN)^s + \gamma r^{s\,a}$			$\rho_M{}^s = \rho_M{}^0 + \alpha' Z_1 + \beta' Z_2 + \gamma' Z_3{}^a$			
Compound	α	β	γ	α	β	γ	α	β	γ	$\rho_M{}^0$	$\alpha'(t_{\alpha'})^b$	$\beta'(t_{\beta'})^b$	$\gamma'(t_{\gamma'})^b$
(**1**)	0.699	0.700	0.148	−0.115	−0.094	0.989	−0.706	0.708	−0.015	0.0016	−0.342 (11.89)	−0.858 (21.85)	0.369 (4.14)
(**2**)	0.707	0.705	0.054	0.008	−0.084	0.996	−0.707	0.704	0.065	0.0012	−0.217 (5.01)	−0.936 (15.59)	−0.174 (0.45)
(**3**)	0.704	0.698	−0.131	0.044	0.141	0.989	−0.709	0.702	−0.068	−0.0017	0.030 (0.648)	−0.969 (15.64)	0.348 (2.52)
(**4**)	0.679	0.656	0.331	−0.155	−0.313	0.937	−0.718	0.687	0.111	−0.0013	−0.601 (21.60)	−0.525 (13.02)	0.399 (4.24)

[a] $(E_T^N)^s$, $(DN)^s$, r^s, and $\rho_M{}^s$ are the standardized variables. [b] t Values.

Table 7. Numerical values of the relationship $\rho_M{}^s = \rho_M{}^0 + a'(E_T^N)^s + b'(DN)^s + c' r_M{}^s$ and percentage contribution from polarity ($\bar{a}$), Lewis basicity ($\bar{b}$), and cation radius ($\bar{c}$) effects in correlations (1) estimated by Principal Component Analysis

	$\rho_M{}^s = \rho_M{}^0 + a'(E_T^N)^s + b'(DN)^s + c' r_M{}^s$						
Compound	$\rho_M{}^0$	a'	b'	c'	$\bar{a}$ (%)	$\bar{b}$ (%)	$\bar{c}$ (%)
(**1**)	0.0016	−0.401	0.103	−0.906	28.4	7.3	64.3
(**2**)	0.0012	−0.160	−0.074	−0.944	13.6	6.3	80.1
(**3**)	−0.0017	−0.269	0.128	−0.986	19.5	9.3	71.2
(**4**)	0.0013	−0.613	0.044	−0.647	47.0	3.4	49.6

variables, the second principal component absorbs the maximum of the remaining variation, and so on.

The variables Z_i were calculated through the matrix of the standardized variables using the package program of the Scientific Library of IBM and are shown in Table 6.

A regression analysis of $\rho_M{}^s$ on the principal components Z_i gives new relationships (5) also included in Table 6. Substituting

$$\rho_M{}^s = \rho_M{}^0 + \alpha' Z_1 + \beta' Z_2 + \gamma' Z_3 \qquad (5)$$

back in these expressions Z_i by use of (4) it is possible to determine the new coefficients a'—c' of the substituents in (6)

$$\rho_M{}^s = \rho_M{}^0 + a'(E_T^N)^s + b'(DN)^s + c' r_M{}^s \qquad (6)$$

which allows the accurate calculation of the relative weights of the different parameters used in the model (1) directly [$\bar{x} = x'/(a' + b' + c') \times 100\%$; $x = a, b, c$].

Table 7 shows the values for relationship (6) and the percentage contributions of the different parameters E_T^N, DN, and r calculated as described above.

From these results we can say that the spin density at the alkali-metal in the ion pairs derived from (**1**)—(**4**) depend both on the solvating power of the solvent and on the nature of the metal ion. Too many different effects are involved in the solvation of ion pairs. The model (1) accounts for both the non-specific solvation as characterized by the polarity parameter E_T^N and the electron pair donation capacity as characterized by DN (since we are dealing with aprotic solvents there is no need for a parameter describing the hydrogen-bonding capacity of the solvent). The high value of $\bar{a}$ as compared with $\bar{b}$ shows that the dipolar interactions with the solvent are dominant by far in the solvation of these ion pairs. This observation shows that in ion pairs derived from strong chelating anions the specific solvation of the cation is much less important than in other ion pairs, *e.g.* in enolates.[24]

The calculated correlations (1) allow a discussion of solvent and cation effects on the structures of these ion pairs, since the variation of the spin density in the alkali-metal ρ_M with the distance r_{OM} between the cation and the oxygen atoms of the radical anion has been calculated.[7,31]

In qualitative terms the effects are easily understood as long as one is not misled by the changing nature of b in the triparametric correlation: b is either positive or negative but always very small (see Table 3). One should however interpret the effect of DN on ρ_M as if b was always negative.

The reason for this can be found in the circumstance that the coefficient of DN is negative in the monoparametric correlation (Table 2) as well as in the diparametric correlations [ρ_M as a function of DN and r_M (Table 5) and ρ_M as a function of E_T^N and DN (not shown in this paper for the sake of brevity)]. In the triparametric correlation only the sign of the coefficient b of DN starts changing from case to case, according to the radical anion [positive for (**1**), (**3**), and (**4**) and negative for (**2**)].

This happens because such a high proportion of the total effect is due to the influence of E_T^N and even more r_M, which leads to much more of the bDN term being absorbed into the other terms (aE_T^N and cr_M) as in the di- and mono-parametric expressions, leading to a bDN term smaller than the error of the approximation.

Why is it then that an increase of either E_T^N, DN, or r_M results in a decrease of the electron spin density ρ_M at the alkali-metal nucleus? Increasing E_T^N means increasing the dipolar interactions and therefore a weakening of the electrostatic attractions. Increasing DN will lead by specific electron pair donation from the solvent to dispersion of its positive charge and therefore also to a weakening of the interionic Coulombic attraction. Both effects will therefore lengthen the interionic distance. As to the effect of r_M, it is already known from the negative temperature gradient and the positive sign of ρ_M[5–7] that in the chelating radical anions of 1,2-diaroylbenzenes the interionic association energy predominates over the solvent–cation interaction. Therefore a larger cation radius will lengthen the interionic distance, contrary to what happens *e.g.* in carbanions or in radical-anions derived from hydrocarbons. The lengthening of the interionic distance will decrease the $\langle n|\pi\rangle$ interaction and therefore ρ_M, explaining the negative sign for the coefficients of E_T^N, DN, and r_M in the most relevant correlations.

The values of the weights of the coefficients, *i.e.* of $\bar{a}$, $\bar{b}$, and $\bar{c}$ are to be found in Table 7. They have to be interpreted cautiously because of the reservations expressed above. Nevertheless it is obvious that with the 1,2,4,5-tetramesitoylbenzene radical anion ($\mathbf{4}^{\bullet -}$) with a wider spread of negative charge, the effect of the solvent dipolarity on the increase of the oxygen metal distance r_{OM} is more important compared with the effect of the cation radius as in the radical anions derived from the other diaroylbenzenes ($\mathbf{1}^{\bullet -}$)—($\mathbf{3}^{\bullet -}$). The differences between the values of $\bar{a}$, $\bar{b}$, and $\bar{c}$ for these last three seem to us too small that an interpretation of such a straightforward kind is reasonable.

The value of correlation (1) is rather to be sought in the circumstance that it can be used for a surprisingly large range of phenomena concerning oxygen-containing organic anions in aprotic solvents as shown in other Parts. The results are consistent as far as they all provide some evidence that the variation in the properties observed is largely a consequence of variations of the interionic distance.

Experimental

1,2-Dimesitoyl- (*o*-DMB) (**1**), 1-benzoyl-2-mesitoyl- (*o*-BMB) (**2**), 1,2-bispentamethylbenzoyl- (*o*-DPMBB) (**3**), and 1,2,4,5-tetramesitoyl-benzene (TMB) (**4**) were synthesized and purified as described elsewhere.[2,4,32,33]

Diethyl ether (DE), dibutyl ether (DBE), 1,4-dioxane (DO), 2-methyltetrahydrofuran (MTHF), tetrahydrofuran (THF), dimethoxyethane (DME), diglyme (DG), triglyme (TG), *NN*-dimethylformamide (DMF), and hexamethylphosphotriamide (HMPA) were dried by known techniques.[24]

All the experimental spin densities of the ion pairs derived from (**1**) with the different alkali-metals are described in the literature.[1,2,4] The spin densities of the ion pairs derived from ($\mathbf{2}^{\bullet -}$) and ($\mathbf{3}^{\bullet -}$) in THF and (**4**) in THF and MTHF are also described in the literature.[2–4] All the other spin densities of (**1**)—(**4**) cited in this work were determined as referred in the foregoing reports.[1–4] The e.s.r. spectra were recorded at room temperature using a Bruker ER 200D spectrometer.

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