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ESR and ENDOR Studies of a Radical Anion with Formally Nonconjugated Keto Groups: *cis*-10,11-Dimethyldiphensuccindan-9,12-dione

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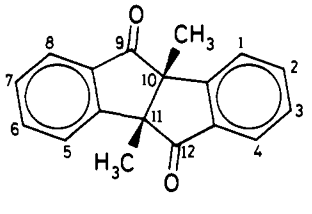
Received August 30, 1978

Abstract: The radical anion of *cis*-10,11-dimethyldiphensuccindan-9,12-dione (**1**), which contains two equivalent, formally nonconjugated monoketone π systems, has been studied by ESR and ENDOR spectroscopy. In the ion pairs formed by $\mathbf{1}^{-}\cdot$ and its counterion, the bulk of the spin population is accommodated on one π moiety, and the cation is situated in the proximity of the pertinent oxygen atom. The rate, k, of interconversion between two such equivalent ion pairs is thus tantamount to the frequencies of both the intramolecular electron transfer and the migration of the cation between the preferred sites at the two oxygen atoms. The dependence of the rate k and the proton coupling constants on the solvent, counterion, and temperature has been investigated in detail. When k lies in the range of 10^6–10^9 s^{-1} it is comparable to the hyperfine time scale, and the ESR spectra exhibit effects of specific line broadening. The activation parameters (solvent, dimethylformamide; counterion, Et_4N^+) for the interconversion are $\Delta H^{\ddagger} = 26$ kJ/mol and $\Delta S^{\ddagger} = 23$ J/(mol K). The proton coupling constants, observed under a variety of experimental conditions, agree excellently with the values calculated with the use of a simple HMO model which treats $\mathbf{1}^{-}\cdot$ as two weakly interacting monoketone π systems.

In a preceding paper,[2] a vibronic model was proposed to account for the unusual IR absorption of the radical anion of *cis*-10,11-dimethyldiphensuccindan-9,12-dione (**1**). The spectroscopic properties of $\mathbf{1}^{-}\cdot$, which contains two formally nonconjugated monoketone fragments, depend critically on the electron exchange between the two equivalent π moieties. Since the frequency of the electron transfer must be in concert with the rate of migration of the counterion between these moieties,[3] the observed hyperfine pattern should be sensitive to the factors affecting the ion pairing, such as the polarity of the solvent, the nature of the counterion, and the temperature. Their role is examined in the present paper, which reports the results of ESR and ENDOR studies of $\mathbf{1}^{-}\cdot$, performed under various experimental conditions.



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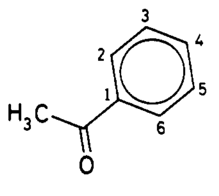

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Experimental Section

The preparation of *cis*-10,11-dimethyldiphensuccindan-9,12-dione has been described elsewhere.[2]

The radical anion $\mathbf{1}^{-}\cdot$ was produced by both "chemical" and electrolytic reduction of **1**. The chemical method consisted in reaction of **1** with potassium, sodium, and lithium in 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), and 2-methyltetrahydrofuran (MTHF); the reaction of **1** with potassium was also carried out in a 2:1 mixture of DME and hexamethylphosphoric triamide (HMPA).

Electrolytic generation of $\mathbf{1}^{-}\cdot$ was achieved in DME, dimethylformamide (DMF), acetonitrile (ACN), and dimethyl sulfoxide (Me_2SO). Tetraethyl- as well as tetra-*n*-butylammonium perchlorate served as the supporting electrolytes in DMF, ACN, and Me_2SO, while in DME, for reasons of solubility, only the tetra-*n*-butylammonium salt could be used. Moreover, the electrolytic reduction in all four solvents was performed with sodium tetraphenylborate, replacing tetraalkylammonium perchlorate as the supporting salt.

In general, the radical anions $\mathbf{1}^{-}\cdot$ prepared under the aforementioned conditions were sufficiently stable for an investigation in the

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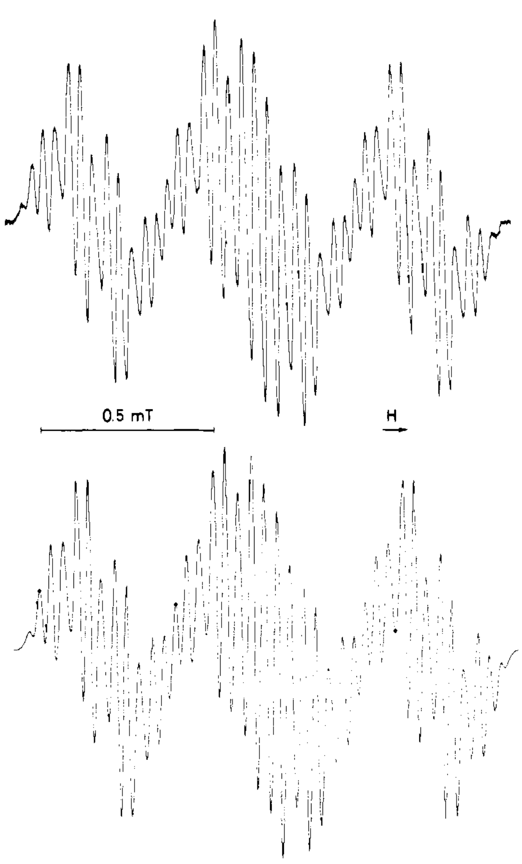


Figure 1. Type *S* ESR spectrum of the radical anion $1^{-}\cdot$. Top: experimental spectrum; solvent, DME; counterion, K^+; temperature, 183 K. Bottom: spectrum simulated with the use of the proton coupling constants listed in Table I; line shape, Lorentzian; line width, 0.012 mT.

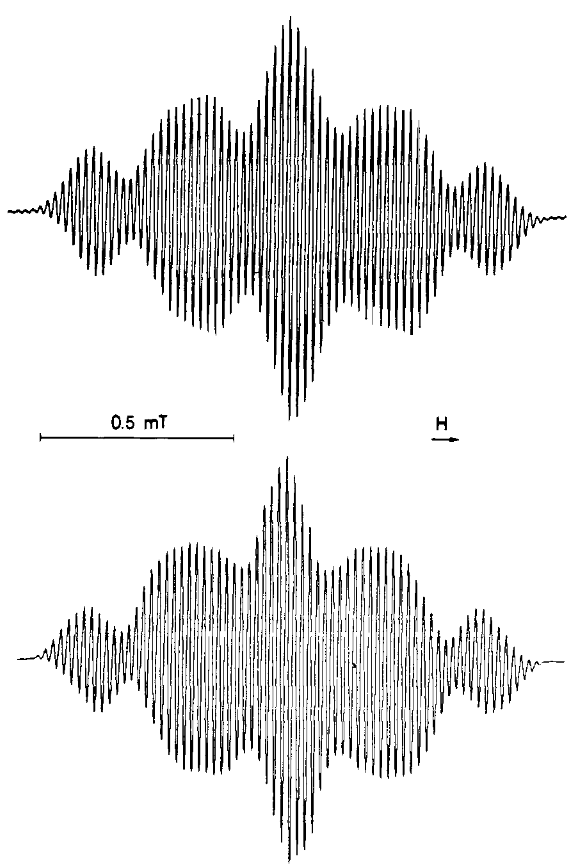


Figure 2. Type *R* ESR spectrum of the radical anion $1^{-}\cdot$. Top: experimental spectrum; solvent, DME/HMPA (2:1); counterion, K^+; temperature, 183 K. Bottom: spectrum simulated with the use of the proton coupling constants listed in Table I; line shape, Lorentzian; line width, 0.010 mT.

temperature range between 293 K and the freezing points of the solutions. Partial conversion into a secondary paramagnetic species, presumably the radical anion of a monoketone, occurred in the DME/HMPA mixture above 203 K, so that the studies in this case were restricted to the low-temperature region.

Whereas the ESR spectra of $1^{-}\cdot$ formed by either method could be investigated in the whole accessible temperature range, the ENDOR studies were practicably possible only for the chemically produced radical anions below 223 K. The ENDOR apparatus used was the Varian E-1700 system linked to a Varian E-9 spectrometer.

Results

Classification and Analyses of the Spectra. Figure 1 shows an ESR spectrum of $1^{-}\cdot$, taken at 183 K upon reaction of **1** with potassium in DME. A dramatic change occurred in the hyperfine pattern when a substantial amount of HMPA was added to DME. Such a change is evident by comparison of the spectrum in Figure 1 with that presented in Figure 2 for $1^{-}\cdot$ in a 2:1 mixture of DME and HMPA. The two types of spectra, exemplified by Figures 1 and 2, will henceforth be denoted as *S* and *R*, respectively. Their analyses were greatly assisted by the ENDOR technique. Figure 3 displays the ENDOR proton signals obtained with the same solutions as those giving rise to the ESR spectra in Figures 1 and 2. The change on passing from the solvent DME (type *S*) to the mixture DME/HMPA (type *R*) is as impressive in the ENDOR as in the ESR spectra. Careful examination of the positions and shapes of the ENDOR signals, combined with a repeated computer simulation of the ESR spectra, yielded finally the proton coupling constants, $a_{H\mu}$, listed in Table I. The accuracy achieved is demonstrated by the close correspondence between the observed ESR spectra and the derivative curves which were computed with the use of these values $a_{H\mu}$, and which are also reproduced in Figures 1 and 2 below the experimental records.

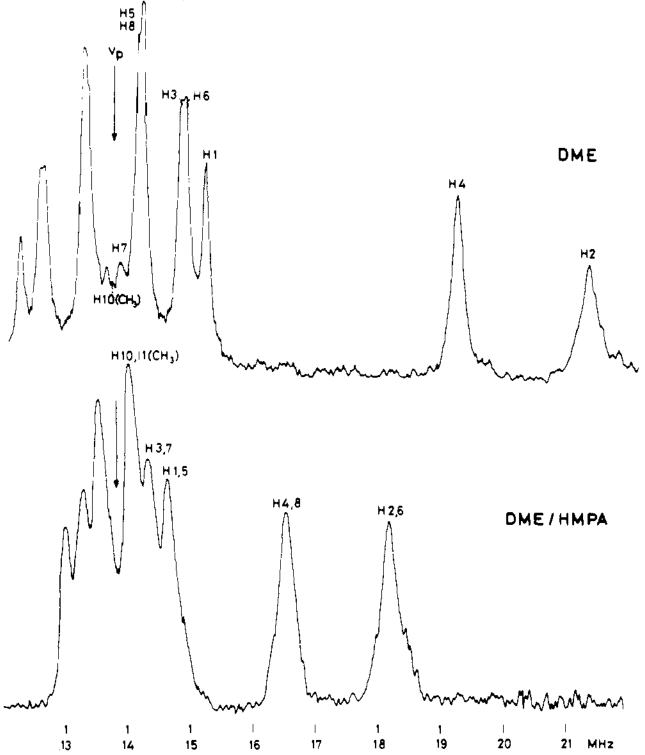


Figure 3. ENDOR spectra of the radical anion $1^{-}\cdot$. Experimental conditions for the top (DME) and bottom spectra (DME/HMPA) are the same as those for the ESR spectra in Figures 1 (type *S*) and 2 (type *R*), respectively. ν_p = frequency of the free proton.

Table I. Comparison of the Proton Coupling Constants, a_{H_μ} (mT), for the Radical Anion of *cis*-10,11-Dimethyldiphensuccindan-9,12-dione (**1**) and Acetophenone (**2**)

		$\mathbf{1}^{-}\cdot$					$\mathbf{2}^{-}\cdot$	
		type *S*		type *R*				
solvent		DME		DME/HMPA	DMF		DME	DMF
counterion		K^+		K^+	Et_4N^+		n-Bu_4N^+	n-Pr_4N^+
temp, K		183		183	293		298	298
position	$\mu = 1$	0.106	0.067^a	0.059	0.060	$\mu = 3$	0.113	0.107
	5	0.028					(0.057)^b	(0.054)^b
	2	0.544	0.313^a	0.312	0.311	4	0.655	0.660
	6	0.082					(0.328)^b	(0.330)^b
	3	0.077	0.043^a	0.040	0.042	5	0.091	0.088
	7	0.009					(0.046)^b	(0.044)^b
	4	0.394	0.221^a	0.193	0.205	6	0.376	0.371
	8	0.028					(0.188)^b	(0.186)^b
	11(CH_3)	0.032	~0.016^a	0.019	0.020			
	10(CH_3)	~0						

^{a} Averaged value. ^{b} Halved value.

In the spectra of type *S* (Figure 1), the coupling constants a_{H_μ} are due to *eight single* protons and *two* sets of *three*, whereas in those of type *R* (Figure 2), they arise from *four* pairs of protons and *one* set of *six*. It is essential to note that the eight one-proton values a_{H_μ} for the type *S* can be grouped pairwise in such a way that the average of each pair of a_{H_μ} approximately matches one of the four two-proton values for the type *R*. The two three-proton values found in the former case are analogously "paired", since their average is nearly equal to the six-proton value obtained in the latter. The arrangement of the coupling constants a_{H_μ} in Table I renders such "pairing" relationships prominent. Experimental evidence for these relationships is provided by the third type of spectra which represents a transition between *R* and *S* and will henceforth be denoted as *I*.

The spectra of type *I* are exemplified by that shown in Figure 4 and taken of electrolytically generated radical anion $\mathbf{1}^{-}\cdot$ in DMF at 213 K (tetraethylammonium perchlorate as the supporting salt). Characteristic of these spectra was a *specific* line broadening, i.e., the line widths differed for individual hyperfine components. Such a phenomenon urged the use of a two-jump model[4] for a pairwise exchange between two sets of coupling constants a_{H_μ}. This model served for the computer simulation of the derivative curve which is also reproduced in Figure 4 and agrees with the experimental spectrum in all essential features. The pairwise exchanging coupling constants a_{H_μ} and the rate, k, of their exchange, employed in the simulation, were obtained from the least-squares fitting procedure;[5] they are given in the caption to Figure 4. It is noteworthy that this simulation requires that the two coupling constants involved in the exchange have, in each case, the same sign. Their values closely parallel those found in the type *S* spectra, and, consequently, the averages of the pairs of a_{H_μ} resemble the hyperfine data for the type *R* (Table I). The similarity is particularly evident when one compares these averages with the coupling constants a_{H_μ} observed for $\mathbf{1}^{-}\cdot$ in the same environment (solvent, DMF; counterion, Et_4N^+), but at higher temperature (293 K). The pertinent coupling constants, indicative of the type *R*, are listed in Table I, along with the analogous values for $\mathbf{1}^{-}\cdot$ in DME/HMPA.

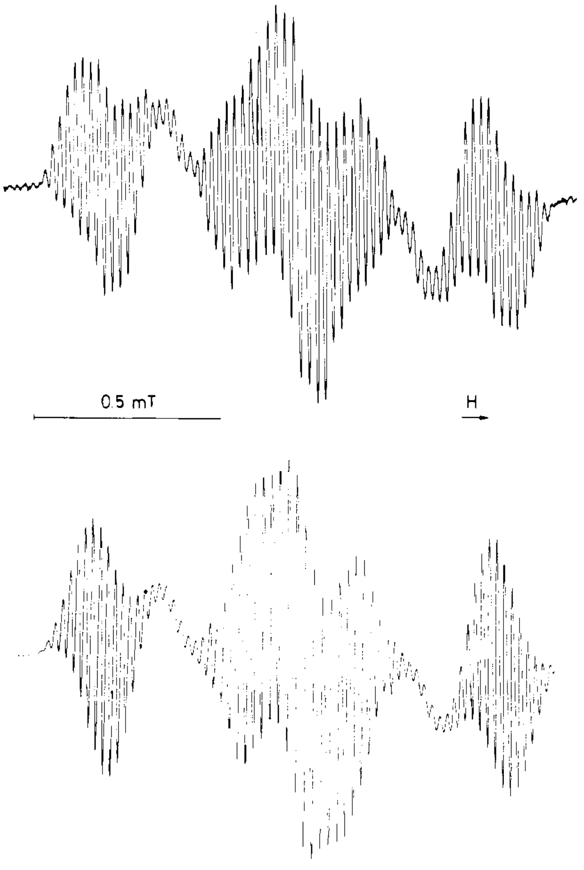


Figure 4. Type *I* ESR spectrum of the radical anion $\mathbf{1}^{-}\cdot$. Top: experimental spectrum; solvent, DMF; counterion, Et_4N^+; temperature, 213 K. Bottom: spectrum simulated with the use of the following pairs of exchanging coupling constants (mT): $a_{H1} = 0.101$ and $a_{H5} = 0.026$; $a_{H2} = 0.540$ and $a_{H6} = 0.084$; $a_{H3} = 0.074$ and $a_{H7} = 0.009$; $a_{H4} = 0.372$ and $a_{H8} = 0.034$; $a_{H11}(CH_3) = 0.038$ and $a_{H10}(CH_3) = 0.003$; exchange rate $k = 2.8 \times 10^7$ s^{-1}; line shape, Lorentzian; line width, 0.010 mT.

Assignment of the Coupling Constants. Apart from the values a_{H_μ}, arranged in accordance with their "pairing" relationships, Table I presents an assignment of these values to protons in the individual positions μ of $\mathbf{1}^{-}\cdot$. This assignment, which underlies the labeling of the ENDOR signals in Figure 3, will be justified below.

For the ring protons in the positions $\mu = 1$–8, the assignment is based on comparison of the values a_{H_μ} for $\mathbf{1}^{-}\cdot$ with the analogous hyperfine data reported for the radical anion of acetophenone (**2**)[6] (Table I). Since $\mathbf{1}^{-}\cdot$ comprises twice the monoketone π system of $\mathbf{2}^{-}\cdot$, the coupling constants found for the four pairs of equivalent ring protons in the spectra of type *R* should be half as large as the corresponding values for $\mathbf{2}^{-}\cdot$. This expectation is fully borne out by experiment if the assignment of the data for the type *R* is exactly the one made in Table I. In the alternative case of type *S*, the assignment is guided by the pairing relationships between the coupling constants a_{H_μ}, whereby the arguments advanced in the Discussion demand that the larger value a_{H_μ} of each pair should

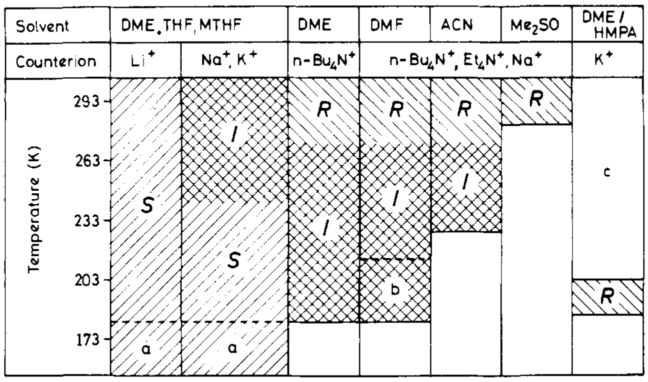


Figure 5. Diagram showing schematically the conditions (solvent, counterion, and temperature) under which spectra of type *S*, *R*, and *I* were observed for the radical anion **1**⁻·. (a) Region below the freezing point of DME; refers to THF and MTHF only. (b) Solidification of DMF prevented by addition of a small amount of ACN. (c) Radical anion unstable (cf. Experimental Section).

Table II. Effect of the Counterion on the Proton Coupling Constants, a_{H_μ} (mT), for the Radical Anion **1**⁻· in DME at 183 K

position	counterion		
	K^+	Na^+	Li^+
μ = 1	0.106	0.111	0.130
5	0.028	0.026	0.024
2	0.544	0.566	0.601
6	0.082	0.064	0.028
3	0.077	0.079	0.084
7	0.009	0.008	0.006
4	0.394	0.414	0.462
8	0.028	0.026	0.015
11(CH_3)	0.032	0.032	0.032
10(CH_3)	~0	~0	~0

be assigned to the ring proton in the same monoketone moiety (μ = 1–4), leaving the smaller one for the proton in the second moiety (μ = 5–8).

In the type *R* spectra, the assignment of the six-proton coupling constant is straightforward, considering the equivalence of the two methyl groups in the positions 10 and 11. It is less secure in the case of the two corresponding three-proton values which appear in the type *S* spectra. For lack of additional evidence, it has been assumed that the larger of the two paired values belongs to the protons of that methyl substituent (position 11) which is separated by a lesser number of bonds from the carbon atom 12 in one C=O group. This atom is a part of the monoketone moiety containing the ring protons with the major coupling constants a_{H_μ} (μ = 1–4), and, according to the HMO model (see Discussion), it should bear, by far, the highest π spin population ($\rho_{12} \approx 0.25$).

Occurrence of the Spectra of Type *S*, *R*, and *I*. Figure 5 provides a survey of the temperature regions where the three types of spectra were observed for **1**⁻· with various solvents and counterions. At this point, it is important to remark that the diagram presented here also holds under conditions where an excess of unreduced diketone **1** was introduced into the solution or where the concentration of the radical anion **1**⁻· and its counterion was considerably increased. In other words, the type of spectrum was essentially not altered by such changes in concentration, the only conspicuous change being an *unspecific* broadening of all hyperfine lines.

In the following, the conditions under which the spectra of type, *S*, *R*, and *I* were obtained, and their effect on the hyperfine patterns of these spectra, are examined in more detail.[7]

Table III. Temperature Dependence of the Proton Coupling Constants, a_{H_μ} (mT), in the Type *S* Spectra of the Radical Anion **1**⁻· (Solvent, MTHF; Counterion, K⁺)

position	temp, K			
	163	183	203	223
μ = 1	0.102	0.106	0.112	0.118
5	0.034	0.028	0.026	0.022
2	0.536	0.544	0.550	0.558
6	0.090	0.082	0.078	0.066
3	0.074	0.077	0.078	0.078
7	0.010	0.009	0.008	0.008
4	0.387	0.394	0.400	0.408
8	0.034	0.028	0.024	0.022
11(CH_3)	0.032	0.032	0.033	0.034
10(CH_3)	~0	~0	~0	~0

Type *S*. Spectra of this type resulted from reaction of **1** with an alkali metal in DME, THF, and MTHF at low temperatures. Provided that the counterion (i.e., the alkali metal used as the reducing agent) and the temperature were the same, the ESR and ENDOR spectra were closely similar, irrespective of the ethereal solvent employed. They afforded, within the limits of the experimental error (±0.001 mT), identical coupling constants a_{H_μ}.

With K^+ or Na^+ as the counterion, the type *S* spectra were observed below 243 K where they depended markedly on temperature. On the other hand, with Li^+, such spectra persisted up to 293 K and displayed only negligible temperature dependence.

The effect of the counterion on the coupling constants in the type *S* spectra is demonstrated in Table II, which lists the values a_{H_μ} for **1**⁻· in DME at a single temperature (183 K), but with different alkali metal cations. On going from K^+ to Na^+ to Li^+, a considerable increase was found in the larger coupling constants a_{H_μ} assigned to the ring protons in the same monoketone moiety (μ = 1–4). However, since this increase occurred partly at the expense of the corresponding paired values for the second moiety (μ = 5–8), the averages of the pairs of a_{H_μ} were less altered than the individual coupling constants.

A similar effect in the type *S* spectra, albeit of smaller magnitude, was brought about by raising the temperature in the region below 243 K when Na^+ or K^+ was the counterion. This effect is evident from Table III where the values a_{H_μ} are given for **1**⁻· in MTHF with the same counterion (K^+), but at temperatures varying from 163 to 223 K.

In no case could splitting from the magnetic nucleus (^7Li, ^{23}Na, and ^{39}K) of the counterion be resolved in the ESR spectrum. The pertinent coupling constants must therefore be considerably smaller than the line width of ca. 0.01 mT.

Type *R*. Apart from **1**⁻· produced chemically in DME/HMPA below 203 K or generated electrolytically in DMF at 293 K, spectra of type *R* were observed upon electrolytic reduction of **1** in ACN or Me_2SO at room temperature. As with the solvent DMF, an alkylammonium perchlorate served as the supporting salt, i.e., Et_4N^+ or *n*-Bu_4N^+ were the counterions. Within the limits of experimental error, the coupling constants found under such conditions for **1**⁻· in ACN and Me_2SO were identical with those obtained for this radical anion in DMF (Table I). The type *R* spectrum was preserved when, through the use of sodium tetraphenylborate as the supporting electrolyte, the counterion Na^+ replaced Et_4N^+ or *n*-Bu_4N^+ in DMF, ACN, and Me_2SO at 293 K.

It is noteworthy that spectra of type *R* were likewise observed upon electrolysis of **1** at 293 K in DME with *n*-Bu_4N^+ as the counterion. Replacement of *n*-Bu_4N^+ by Na^+ led, however, under these conditions not to the spectrum of type

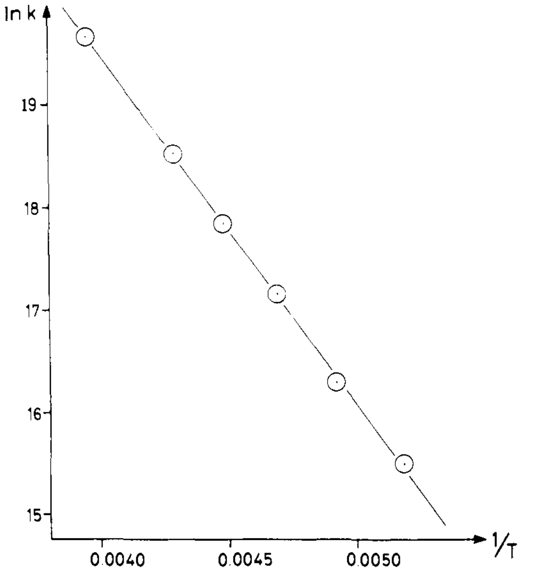


Figure 6. Arrhenius plot for the rate, k, of exchange between the paired coupling constants a_{H_μ}: solvent, DMF; counterion, $\mathrm{Et_4N^+}$.

Table IV. Activation Parameters for the Exchange between the Paired Coupling Constants a_{H_μ} (Solvent, DMF; Counterion, $\mathrm{Et_4N^+}$)

log A	E_a, kJ/mol	$\Delta H^{\ddagger}$, kJ/mol	$\Delta S^{\ddagger}$, J/(mol K)	$\Delta G^{\ddagger}$, kJ/mol
14.4 ± 0.6	28.6 ± 2.5	26.1 ± 2.5	23 ± 8	19.0 ± 0.6

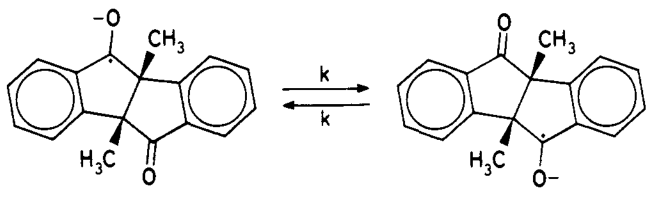
R, but to that of type I (also observed upon chemical reduction of **1** with sodium in DME at the same temperature; see below).

Type *I*. Figure 5 shows that spectra of this type could be obtained starting from those of either type S or R by respectively raising or lowering the temperature. As pointed out in the previous section, the type I spectra exhibited *specific* line broadening, and their analyses implied the use of a two-jump model for two sets of pairwise exchanging coupling constants. The procedure, which involved least-squares fittings of the derivative curves, has been illustrated by the spectrum taken at 213 K of the electrolytically generated radical anion in DMF (Figure 4). It was also applied to other spectra of type I which were observed for $\mathbf{1}^{-}\cdot$ in DMF with the same counterion ($\mathrm{Et_4N^+}$) between 193 and 253 K (whereby addition of a small amount of ACN to DMF at the lowest temperatures prevented the freezing of the solution). These spectra proved to be particularly suited for a detailed study of the line-width effects. They yielded the exchange rates $k = 5.3 \times 10^6$, 1.2×10^7, 5.6×10^7, 1.1×10^8, and $3.5 \times 10^8\ \mathrm{s^{-1}}$ at the temperatures $T =$ 193, 203, 223, 233, and 253 K, respectively, in addition to the value $k = 2.8 \times 10^7\ \mathrm{s^{-1}}$ determined at 213 K (cf. caption to Figure 4). Figure 6 presents the Arrhenius plot of ln k vs. $1/T$; the pertinent activation parameters are listed in Table IV.

Discussion

General Interpretation. The observation of the three types of spectra, S, R, and I, for the radical anion $\mathbf{1}^{-}\cdot$ is readily rationalized in terms of two interconverting equivalent structures $\mathbf{1a}^{-}\cdot$ and $\mathbf{1b}^{-}\cdot$ in which the bulk of the spin population is localized on one monoketone π system.

The interconversion $\mathbf{1a}^{-}\cdot \rightleftharpoons \mathbf{1b}^{-}\cdot$ involves two concerted phenomena:[3] (1) transfer of the unpaired electron between the two equivalent, formally nonconjugated π systems and (2) migration of the counterion between two preferred sites in these systems. Since the rate, k, of the interconversion is inversely proportional to the lifetime, τ, of the ion pair, it depends on the strength of association of the counterion with the radical anion.



$\mathbf{1a}^{-}\cdot$ $\mathbf{1b}^{-}\cdot$

For tight ion pairs, the rate $k = 1/\tau$ is relatively low. This means that the interconversion $\mathbf{1a}^{-}\cdot \rightleftharpoons \mathbf{1b}^{-}\cdot$ is *slow* on the hyperfine time scale ($k < 10^6\ \mathrm{s^{-1}}$) and, as a consequence, one encounters spectra of type S characteristic of an individual structure $\mathbf{1a}^{-}\cdot$ or $\mathbf{1b}^{-}\cdot$ (Figure 1). The substantial localization of the π spin population on one monoketone moiety in such a structure is indicated by the coupling constants a_{H_μ} which are larger by an order of magnitude for the ring protons in this moiety ($\mu = 1\text{–}4$) than for their counterparts in the second moiety ($\mu = 5\text{–}8$).

For loose ion pairs, the rate k is considerably higher and the interconversion $\mathbf{1a}^{-}\cdot \rightleftharpoons \mathbf{1b}^{-}\cdot$ becomes *rapid* on the hyperfine time scale ($k > 10^9\ \mathrm{s^{-1}}$). Accordingly, one observes spectra of type R (Figure 2) in which the coupling constants a_{H_μ} are averaged pairwise and the π spin population appears to be evenly distributed between the two monoketone moieties.

When k lies in the *intermediate* range, it is comparable to the hyperfine time scale and ESR spectra of type I (Figure 4) appear. The specific broadening of hyperfine components in these spectra renders them diagnostic of the exchange rate k.

Clearly, the factors which govern the lifetime, τ, of the ion pair, and therewith the rate, k, of the interconversion $\mathbf{1a}^{-}\cdot \rightleftharpoons \mathbf{1b}^{-}\cdot$, should also be responsible for the occurrence of the various types of spectra. These factors are the solvent, the counterion, and the temperature.

Effect of the Solvent. With respect to their influence on the lifetime, τ, of the ion pair, the solvents used in the present studies can be divided into two groups: (1) the ethereal solvents, DME, THF, and MTHF, with a rather low dielectric constant ϵ (<10), and (2) the polar solvents, HMPA, DMF, ACN, and $\mathrm{Me_2SO}$, with a substantially higher value of ϵ (>30).

In the ethereal solvents, long-lived or tight ion pairs are formed. It is noteworthy that, all other factors being the same, the association between the radical anion and the alkali metal cation is equally strong in DME, THF, and MTHF. This behavior contrasts with that of the ion pairs formed by the radical anions of aromatic hydrocarbons where the strength of the association with the alkali metal counterion increases in the order DME < THF < MTHF.[8] The leveling in the response of $\mathbf{1}^{-}\cdot$ to the nature of the ethereal solvent is best rationalized by the structure of the ion pairs of $\mathbf{1}^{-}\cdot$, which is fundamentally different from that of the ion pairs of hydrocarbon radical anions. In the latter, the counterion is embedded in the π cloud of the aromatic system, being situated above the molecular plane at a distance of ca. 300 pm.[9] Its solvation by the ether is of prime importance in this case, and, therefore, the strength of its association with the radical anion decreases on going from MTHF to THF and to DME which complexes the cation in a chelate-like fashion. In the ion pairs of $\mathbf{1}^{-}\cdot$, on the other hand, as in those of most ketyl radical anions, the preferred site of the counterion is undoubtedly in the molecular plane where it closely contacts a lone pair of the oxygen atom[10] and is considerably less prone to changes in the solvation by the ether.

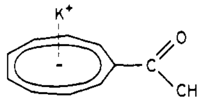
Short-lived or loose ion pairs must prevail in the polar solvents. As exemplified by the 2:1 mixture of DME and HMPA,

Table V. Calculated Ring Proton Coupling Constants, a_{H_μ} (mT), for the HMO Model of the Radical Anion **1**$^{-}\cdot$

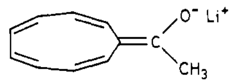
	δ					
position	0	0.1	0.2	0.3	0.4	0.5
μ = 1	+0.057	+0.080	+0.093	+0.101	+0.107	+0.111
5	+0.057	+0.035	+0.021	+0.014	+0.009	+0.007
2	−0.318	−0.458	−0.533	−0.565	−0.579	−0.583
6	−0.318	−0.173	−0.093	−0.055	−0.036	−0.025
3	+0.038	+0.063	+0.080	+0.091	+0.099	+0.104
7	+0.038	+0.018	+0.008	+0.003	+0.001	0.000
4	−0.184	−0.280	−0.340	−0.373	−0.392	−0.406
8	−0.184	−0.097	−0.049	−0.028	−0.018	−0.012

this statement also holds for mixtures of nonpolar with polar solvents, since the ion pairs are preferentially solvated by the molecules of the latter.[11] The similar behavior of **1**$^{-}\cdot$ in DMF, ACN, and Me_2SO is not surprising, in view of the nearly equal dielectric constants ($\epsilon \approx 40$) and comparable solvating power.

Effect of the Counterion. The important role played by the counterion manifests itself both in the interconversion rate, $k = 1/\tau$, of the ion pairs and in the hyperfine data. The dependence of k on the nature of the counterion is evident from Figure 5, which shows that, with DME as the solvent, the temperature required to render k observable on the hyperfine time scale is raised in the order $n\text{-}Bu_4N^+ < K^+ \approx Na^+ < Li^+$. The influence of the counterion on the hyperfine data (Table II) points to an enhanced localization of the π spin population on one monoketone moiety in the order $K^+ < Na^+ < Li^+$. Both effects indicate that the strength of the association between the radical anion **1**$^{-}\cdot$ and its counterion increases with the decreasing size of the cation. Such a finding contrasts with the behavior of the ion pairs of the radical anions of aromatic hydrocarbons, which become tighter in the order $Li^+ < Na^+ < K^+$.[12] It is again the different structure of the ion pairs which accounts for this reversal. The radical anion of an aromatic hydrocarbon, to which the counterion is attached via the π cloud, should be considered as a *soft* base and thus favor the association with a *softer* acid like K^+.[13] In contrast, the radical anion **1**$^{-}\cdot$, where the counterion contacts the lone pair of an oxygen atom, may be regarded as a *hard* base with the preference for a *harder* acid like Li^+. A striking confirmation of such a rationale is a recent report[14] that the electronic structure of the anion **3**$^-$ is a function of the counterion. With π-bonded K^+ an "aromatic" [9]annulenyl (**3a**$^-$) is formed, whereas with Li^+, linked to the oxygen lone pair, an "olefinic" nonafulvene-like ketyl (**3b**$^-$) results.



3a$^-$



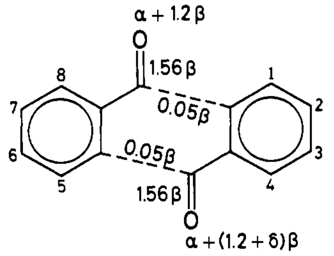
3b$^-$

The effect of the counterion is most pronounced in the ethereal solvents. It levels out in polar solvents; thus in DMF, ACN, and Me_2SO—in contrast to DME—identical spectra are observed with either Na^+ or $n\text{-}Bu_4N^+$.

Temperature Dependence. Raising of the temperature leads to a shortening of the lifetime, τ, of the ion pair and thus to a higher interconversion rate k. The stronger the association between the counterion and the radical anion, the higher the temperature required to bring the rate k into the frequency range comparable to the hyperfine time scale (10^6–10^9 s^{-1}). This temperature, at which the spectra of type *S* change into those of type *I*, lies below 183 K for DMF (containing a few drops of ACN), irrespective of the counterion used. It rises to 243 K for ethereal solvents with Na^+ or K^+ as the counterion, and it exceeds 293 K when these cations are replaced by Li^+ (Figure 5).

The changes in the coupling constants a_{H_μ}, observed for the type *S* spectra with ethereal solvents and alkali metal cations below 243 K (Table III), deserve some comment. In this range of slow interconversion, the most evident effect of raising the temperature is a slight reduction in the low dielectric constants, ϵ, of the solvents. Such a reduction favors the association of the cation with the radical anion and manifests itself by a more pronounced localization of the π spin population on one monoketone moiety. Consequently, the coupling constants a_{H_μ} change in the same direction as with the decreasing size of the cation (see above). The effect is, however, relatively small and restricted to Na^+ and K^+ as the counterions. In the case of Li^+, where the association is extremely tight, the ion pairs are insensitive to the variations in ϵ, and the values a_{H_μ} do not depend significantly on temperature. It is reasonable to assume that above 243 K the influence of slight changes in ϵ on the lifetime, τ, of the ion pairs in the ethereal solvents—and therewith on the rate, k, of interconversion—becomes negligible.

HMO Model. The simplest theoretical treatment of the radical anion **1**$^{-}\cdot$ is provided by a HMO model of two weakly interacting π systems. In the present paper, such an interaction was introduced through bond parameters β' ($= 0.05\beta$) linking each of the carbon centers in the C=O group of one system with an ortho position of the second system.



All the remaining atom and bond parameters retained their standard values, with the exception of those of the two oxygen atoms and the two C=O bonds for which the values suggested by Vincow and Fraenkel[15] were adopted ($\alpha_{\mathrm{O}} = \alpha + 1.2\beta$ and $\beta_{\mathrm{CO}} = 1.56\beta$). The HMO model served for the calculation of the π spin populations ρ_μ, according to the McLachlan procedure[16] ($\lambda = 1.0$). Subsequently, the numbers ρ_μ at the proton-bearing centers μ = 1–8 were converted into the coupling constants a_{H_μ} by means of the McConnell equation[17]

$$a_{\mathrm{H}_\mu} = Q\rho_\mu$$

with $Q = -2.7$ mT. The resulting values a_{H_μ} are listed in Table V under $\delta = 0$; they agree excellently with their experimental counterparts for the spectra of type *R* (Table I).

A slight modification of this HMO model suffices to mimic the coupling constants a_{H_μ} for the spectra of type *S* as well. It consists in an enhancement of the electronegativity of that oxygen atom which is considered as the preferred site of the counterion in $\mathbf{1a}^{-}\cdot$ or $\mathbf{1b}^{-}\cdot$. Such an enhancement is readily taken into account by setting the parameter α_O of this oxygen atom equal to $\alpha + (1.2 + \delta)\beta$ with $\delta > 0$. The coupling constants a_{H_μ} of the ring protons, calculated with $0.1 < \delta < 0.5$ by the same procedure as mentioned above ($\delta = 0$), are also given in Table V. They correlate nicely with their experimental counterparts found in the spectra of type *S* for the eight single ring protons (Table I). Moreover, the effect of increasing δ from 0.2 to 0.5 reproduces the trend in the paired coupling constants a_{H_μ} when K^+ is replaced by Na^+ and Li^+ as the counterion (Table II) or when the temperature is raised from 163 to 223 K (Table III).

The HMO model thus supports a structure of the ion pair in which the substantial localization of the π spin population on one of the two weakly interacting monoketone moieties is brought about by a close contact of the positively charged counterion with the oxygen atom in this moiety.

Concluding Remarks. The results of ESR and ENDOR studies reported above provide some insight into the mechanism of the electron transfer between the two formally nonconjugated π systems of the radical anion of *cis*-10,11-dimethyldiphensuccindan-9,12-dione (**1**). These results, in particular the *specific* line broadening in the type *I* spectra, leave no doubt with respect to the *intra*molecular character of such a transfer.[18] It is reasonable to assume that the counterion migration also takes place within the one and the same ion pair. This assumption is fully justified by the high dilution of the solutions (ca. 10^{-5} mol/dm^3) and is clearly supported by the finding that an increase in the concentration of $\mathbf{1}^{-}\cdot$ and its counterion does not change the type of the spectrum. Molecular models indicate that the migration of the cation between the preferred sites in the proximities of the two oxygen atoms is facilitated by the cis arrangement of the methyl groups.

The rates, $10^6\ s^{-1} < k < 10^9\ s^{-1}$, of the interconversion $\mathbf{1a}^{-}\cdot \rightleftharpoons \mathbf{1b}^{-}\cdot$, which have been found for the type *I* spectra with the solvent dimethylformamide, compare favorably with the analogous values reported for the *intra*molecular electron transfer in the ion pairs of the radical anions containing two phthalimide π systems separated by an alkyl chain.[19] The activation enthalpy, $\Delta H^{\ddagger} = 26$ kJ/mol, can be considered as the energy needed to separate the counterion (Et_4N^+) from the radical anion in the ion pairs of $\mathbf{1a}^{-}\cdot$ or $\mathbf{1b}^{-}\cdot$. Since in DMF such ion pairs are loose, this value represents rather a lower limit to $\Delta H^{\ddagger}$, and considerably higher activation enthalpies are expected with ethereal solvents where tight ion pairs are formed between the radical anion and its counterion. The positive sign of the activation entropy, $\Delta S^{\ddagger} = 23$ J/(mol K), means that, even in DMF, the gain achieved by separating the cation from the radical anion exceeds the loss caused by the increased solvation of the ions by the molecules of the solvent.

Acknowledgment. This work was supported by the Swiss National Science Foundation (Project 2.711.77).

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Calculated Infrared and Raman Spectra of the ^1A_g Ground States of Rectangular Cyclobutadiene and Tetradeuteriocyclobutadiene

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Abstract: The IR fundamental frequencies were calculated for the rectangular ^1A_g ground states of cyclobutadiene and tetradeuteriocyclobutadiene using a single configuration SCF STO-4G basis and were found to be in good agreement with those observed experimentally for cyclobutadiene by Masamune and co-workers and with the previous calculations of Kollmar and Staemmler. Calculated IR intensities and Raman frequencies were also reported.

The observed IR spectrum of cyclobutadiene has been interpreted as indicating a square-planar structure for the molecule, originally because the number of bands agreed with the number expected,[1] and later because the frequencies also agreed with those calculated theoretically for a square ground state.[2] However, several good ab initio calculations of the ge-

0002-7863/79/1501-2281$01.00/0