129. Radical Anions of Polyalkylazulenes: An ESR and ENDOR Study

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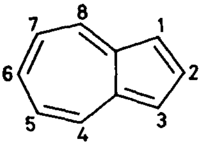
Proton-hyperfine data are reported for the radical anions generated from azulene (**1**) and its alkyl derivatives **2**–**11** in 1,2-dimethoxyethane both 'chemically' with K and electrolytically. The alkyl derivatives are 1,3-dimethyl- (**2**), 5,7-dimethyl- (**3**), 1,3,5,7-tetramethyl- (**4**), 2-methyl- (**5**), 4,6,8-trimethyl- (**6**), 2,4,6,8-tetramethyl- (**7**), 1,3,4,6,8-pentamethyl- (**8**), 1,3,4,8-tetramethyl-6-propyl- (**9**), 6-(*tert*-butyl)-1,3,4,8-tetramethyl- (**10**), and 1,2,3,4,6,8-hexamethylazulene (**11**). Alkyl substituents at the odd-numbered centers $\mu = 1, 3, 5$, and 7 partly shift the π-spin population from the seven- to the five-membered ring, whereas those at the even-numbered centers $\mu = 4, 6$, and 8 exert an opposite effect on the π-spin distribution.

Introduction. – Azulene (**1**) is presumably the most interesting of simplest nonalternant hydrocarbons [1]. Its outstanding features are the blue color, marked basicity [1a], appreciable dipole moment [2], and ease of reduction [3] [1a]. The radical anions of **1** and its 4,6,8-trimethyl derivative (**6**), generated electrolytically in *N,N*-dimethylformamide (DMF), have been studied by ESR spectroscopy in 1962 [4]. Later on, $\mathbf{1}^{-\bullet}$ was also obtained by alkali-metal reduction in 1,2-dimethoxyethane (DME) [5][6] and THF [5b]. Because nonalternant hydrocarbons respond more strongly to perturbations than their alternant analogues, the π-spin distribution in $\mathbf{1}^{-\bullet}$ is sensitive to the association with the positively charged counterion [5][7] and it should likewise be so in regard to the alkyl substitution.

Recently, azulenes bearing four to six Me groups, have become synthetically available [8]. Here, we report the hyperfine data for the radical anions, $\mathbf{1}^{-\bullet}$–$\mathbf{11}^{-\bullet}$ as studied by ESR, ENDOR, and TRIPLE-resonance spectroscopy. For the sake of comparison, the ESR spectra of $\mathbf{1}^{-\bullet}$ and $\mathbf{6}^{-\bullet}$ have been re-examined under the conditions applied to the remaining radical anions.



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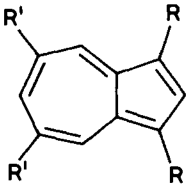

2 R = Me, R' = H
3 R = H, R' = Me
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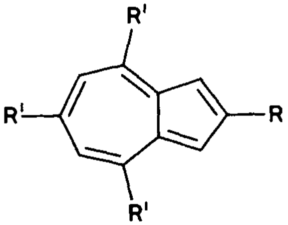

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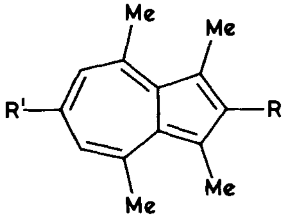

8 R = H, R' = Me
9 R = H, R' = Me(CH$_2$)$_2$
10 R = H, R' = Me$_3$C
11 R = R' = Me

Experimental. – Syntheses of **2**–**5** and **7**–**11** are described in [8] (for preparation of **6**, see, *e.g.*, [9]). The compounds were reduced in DME at 195 K both 'chemically' with K metal and electrolytically at a helical cathode of amalgamated gold with a platin wire as the counter-electrode [10] and Bu$_4$NClO$_4$ (0.1M) as the supporting salt. The radical anions thus obtained were stable below 243 K, but slowly decayed at higher temperatures. Their ESR spectra were recorded on a *Varian-E9*-instrument, while a *Bruker-ESP-300*-system served for ENDOR and TRIPLE-resonance studies.

Results. – The radical anions $\mathbf{1}^{-\cdot}$–$\mathbf{11}^{-\cdot}$ gave rise to well-resolved ESR spectra which were taken at 193 K. 'Chemically' generated radical anions were amenable to studies by ENDOR and TRIPLE-resonance spectroscopy [11]. Analysis of the ESR spectra was confirmed by computer-simulation, using the proton-coupling constants determined from the ENDOR signals as the starting parameters which were subsequently refined by a fitting procedure [12]. *Figs. 1* and *2* show the ESR and ENDOR spectra of $\mathbf{11}^{-\cdot}$ as an illustrative example, while the hyperfine data for all radical anions $\mathbf{1}^{-\cdot}$–$\mathbf{11}^{-\cdot}$ are compiled in *Table 1*. For $\mathbf{1}^{-\cdot}$ with the counterion K$^+$, these values are, in the limits of experimental error, equal to those reported in [6b] and obtained under the same conditions.

Assignments of the coupling constants a_{H_μ} to the α- or Me β-protons[1]) in the positions μ follow the well established sequence [4–7]: $|a_{H1,3}| < |a_{H5,7}| < |a_{H2}| < |a_{H4,8}| < |a_{H6}|$. For $\mathbf{9}^{-\cdot}$, due to the preferred conformation of the 6-propyl substituent, the coupling constant a_{H_μ} of the two CH$_2$ β-protons is half as large as the corresponding value for the three β-protons in the free rotating Me group of $\mathbf{8}^{-\cdot}$ The signs of a_{H_μ} have been based on the results of the general-TRIPLE-resonance experiment, along with the reasonable assumption that those of the absolutely largest values (μ = 2, 4, 6, and 8) are negative for the α- and positive for

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[1]) In ESR spectroscopy, protons separated from a π-center by 0,1,2,... sp^3-hybridized C atoms are denoted α, β, γ, ...

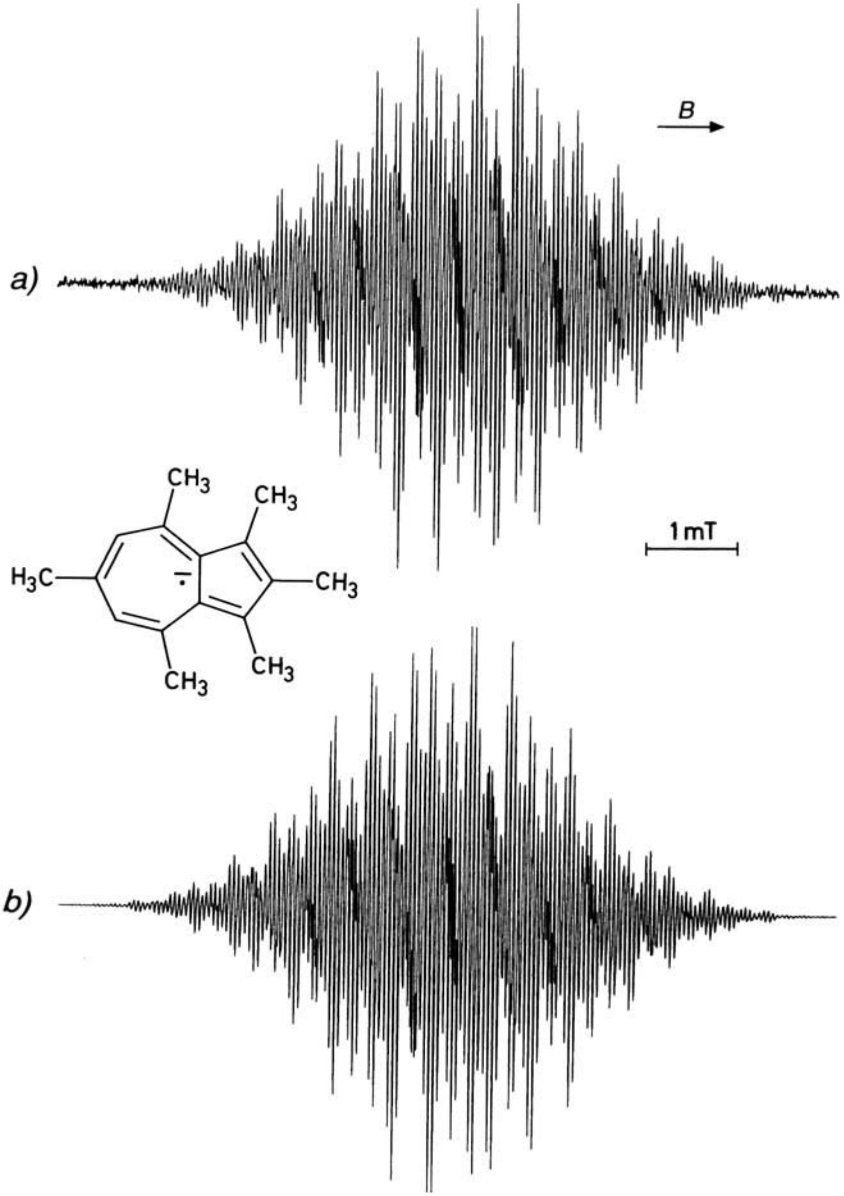

Fig. 1. a) *ESR Spectrum of* **11**$^{-\bullet}$. Solvent: DME; counterion: K$^+$; temp.: 193 K. b) *Simulation*. Coupling constants: *Table 1*; line-shape: *Lorentz*ian; line-width: 0.024 mT

the *β*-protons (see below). It is noteworthy, that the signs of the *γ*-proton-coupling constants turn out to be opposite for the 6-propyl and the 6-*tert*-butyl substituent in **9**$^{-\bullet}$ and **10**$^{-\bullet}$, respectively.

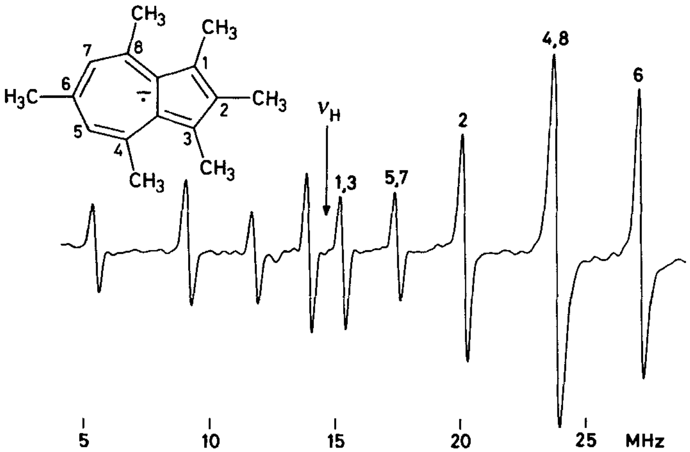

Fig. 2. *Proton-ENDOR spectrum of* $\mathbf{11}^{-\cdot}$ *taken under the same conditions as the ESR spectrum in* Fig. 1

Table 1. *Proton-Coupling Constants,* a_{H_μ} [mT][a]), *for* $\mathbf{1}^{-\cdot}$–$\mathbf{11}^{-\cdot}$ *in DME at 193 K*

	Counterion	μ					
		1, 3	2	4, 8	5, 7	6	
$\mathbf{1}^{-\cdot}$	K^+	+0.027(2 α-H)	–0.397(1 α-H)	–0,613(2 α-H)	+0.122(2 α-H)	–0.875(1 α-H)	
	Bu_4N^+	+0.025	–0.393	–0.625	+0.129	–0.884	
$\mathbf{2}^{-\cdot}$	K^+	–0.064(6 β-H)	–0.432(1 α-H)	–0.601(2 α-H)	+0.114(2 α-H)	–0.865(1 α-H)	
	Bu_4N^+	–0.063	–0.430	–0.605	+0.116	–0.866	
$\mathbf{3}^{-\cdot}$	K^+	+0.023(2 α-H)	–0.402(1 α–H)	–0.595(2 α-H)	–0.100(6 β-H)	–0.856(1 α-H)	
	Bu_4N^+	+0.022	–0.391	–0.610	–0.106	–0.865	
$\mathbf{4}^{-\cdot}$	K^+	–0.057(6 β-H)	–0.429(1 α-H)	–0.570(2 α-H)	–0.089(6 β-H)	–0.822(1 α-H)	
	Bu_4N^+	–0.057	–0.429	–0.587	–0.097	–0.845	
$\mathbf{5}^{-\cdot}$	K^+	+0.031(2 α-H)	+0.449(3 β-H)	–0.597(2 α-H)	+0.113(2 α-H)	–0.861(1 α-H)	
	Bu_4N^+	+0.031	+0.446	–0.608	+0.117	–0.866	
$\mathbf{6}^{-\cdot}$	K^+	+0.013(2 α-H)	–0.376(1 α-H)	+0.658(6 β-H)	+0.153(2 α-H)	+0.934(3 β-H)	
	Bu_4N^+	+0.013	–0.368	+0.670	+0.153	+0.939	
$\mathbf{7}^{-\cdot}$	K^+	+0.023(2 α-H)	+0.423(3 β-H)	+0.642(6 β-H)	+0.134(2 α-H)	+0.912(3 β-H)	
	Bu_4N^+	+0.020	+0.416	+0.655	+0.139	+0.920	
$\mathbf{8}^{-\cdot}$	K^+	–0.043(6 β-H)	–0.327(1 α-H)	+0.664(6 β-H)	+0.182(2 α-H)	+0.911(3 β-H)	
	Bu_4N^+	–0.042	–0.321	+0.673	+0.195	+0.912	
$\mathbf{9}^{-\cdot}$	K^+	–0.045(6 β-H)	–0.331(1 α-H)	+0.663(6 β-H)	+0.174(2 α-H)	+0.489(2 β-H)	–0.030(2 γ-H)
	Bu_4N^+	–0.045	–0.327	+0.680	+0.184	+0.507	–0.030
$\mathbf{10}^{-\cdot}$	K^+	–0.043(6 β-H)	–0.334(1 α-H)	+0.652(6 β-H)	+0.201(2 α-H)		+0.016(9 γ-H)
	Bu_4N^+	–0.041	–0.331	+0.664	+0.226		+0.021
$\mathbf{11}^{-\cdot}$	K^+	–0.048(6 β-H)	+0.392(3 β-H)	+0.649(6 β-H)	+0.203(2 α-H)	+0.883(3 β-H)	
	Bu_4N^+	–0.047	+0.390	+0.663	+0.230	+0.888	

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[a]) Experimental error: ±0.002 mT in $|a_{H_\mu}| > 0.1$ mT and ±0.001 mT in $|a_{H_\mu}| < 0.1$ mT. g Factor = 2.00275±0.00005, throughout.

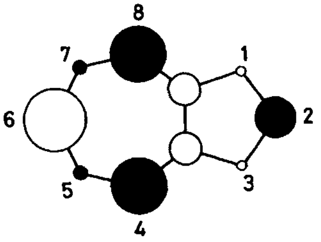


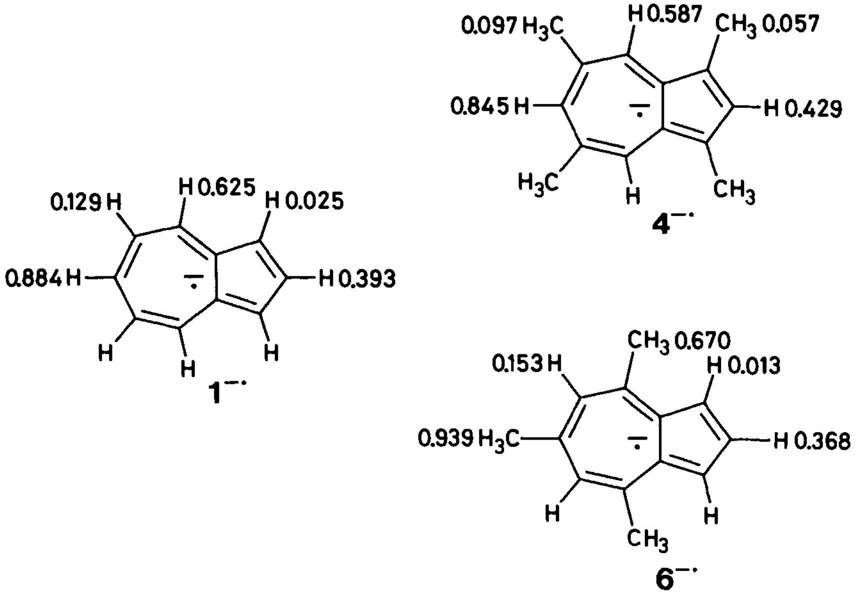
Fig. 3. *Diagram of the LUMO (ψ_6) of* **1**

Discussion. – The $c_{6\mu}^2$ values at the proton-bearing centers μ for the LUMO ψ_6 of **1** fall into two distinct groups (*Fig. 3*); they are large for μ = 2, 4, 6, and 8, but small for μ = 1, 3, 5, and 7. Accordingly, the *even*-numbered centers accomodate high and positive π-spin populations ρ_μ, whereas such populations are small at the *odd*-numbered ones and, due to π,π-spin polarization [13a], they have a negative sign [4]. Upon conversion to the coupling constants $a_{H\mu}$, the sign of ρ_μ is preserved for the β-protons but it is reversed for the α-protons [13b]. However, because the conversion factors have almost the same absolute value for the β-protons in a freely rotating Me substituent and for the replaced α-proton at the π-center μ of a radical anion, the coupling constants $|a_{H\mu}|$ of both proton sorts can serve as a measure of the pertinent π-spin population ρ_μ, irrespective of their opposite signs.

The $|a_{H\mu}|$ values vary considerably according to the positions of the Me substitution, as illustrated in *Fig. 4* by the hyperfine data for $\mathbf{1}^{-\bullet}$, $\mathbf{4}^{-\bullet}$, and $\mathbf{6}^{-\bullet}$.

In $\mathbf{2}^{-\bullet}$–$\mathbf{4}^{-\bullet}$, only the odd-numbered centers μ are Me substituted. Introduction of Me groups at μ = 1 and 3 ($\mathbf{2}^{-\bullet}$) leads to some decrease in the $|a_{H\mu}|$ values at the seven-membered ring and to an increase in such values at the five-membered one. An even stronger decrease in the $|a_{H\mu}|$ values at the seven-membered ring is observed upon Me substitution at μ = 5 and 7 ($\mathbf{3}^{-\bullet}$), while those at the five-membered ring remain almost unchanged relative to $\mathbf{1}^{-\bullet}$. The effects are additive and thus, when all odd-numbered centers μ = 1, 3, 5, and 7 ($\mathbf{4}^{-\bullet}$) bear Me groups, there is a substantial decrease in the $|a_{H\mu}|$ values at the seven-membered ring and a distinct increase in those at the five-membered one (*Fig. 4*).

In $\mathbf{5}^{-\bullet}$–$\mathbf{7}^{-\bullet}$, the Me substitution is confined to the even-numbered centers μ. The main consequence of the introduction of a Me group at μ = 2 ($\mathbf{5}^{-\bullet}$) is an increase of the $|a_{H2}|$ value in this position. With the Me substitutions at μ = 4, 6, and 8 ($\mathbf{6}^{-\bullet}$), the effect turns to be opposite to that of such substitutions at the odd-numbered centers μ. This means that values $|a_{H\mu}|$ considerably increase at the seven-membered ring, but decrease at the five membered one (*Fig. 4*). As the effects are again additive, the overall result for the Me substitution at μ = 2, 4, 6, and 8 ($\mathbf{7}^{-\bullet}$) is a marked increase of the $|a_{H\mu}|$ values at the seven-membered ring and a decrease at μ = 1 and 3 in the five-membered one. The $|a_{H2}|$ value still remains enhanced relative to $\mathbf{1}^{-\bullet}$. The most obvious cause of this enhancement is the inadequacy of the assumption that the factors converting the π-spin populations ρ_μ into $|a_{H\mu}|$ have almost the same absolute value for α- and Me β-protons at all centers μ. Actually, the hyperfine data in *Table 1* suggest that this assumption does not strictly hold for μ = 1, 2, and 3 at the five-membered ring, in which case the conversion factor appears to be substantially larger for the Me β-protons. In contrast to $|a_{H1,3}|$, for which the increase



$1^{-\cdot}$ $4^{-\cdot}$ $6^{-\cdot}$

Fig. 4. *Comparison of the proton-hyperfine data*, $|a_{H\mu}|$ [mT], *for* $\mathbf{1}^{-\cdot}$, $\mathbf{4}^{-\cdot}$, *and* $\mathbf{6}^{-\cdot}$. Solvent: DME; counterion: Bu_4N^+; temp.: 193 K.

on Me substitution works in the same direction as such substitutions at the odd-numbered centers μ, the analogous increase in $|a_{H2}|$ outweighs the decrease brought about by the introduction of the Me groups at the even-numbered centers μ.

Keeping all these arguments in mind, the seeming exception for μ = 2 may be considered as proving the rule that a *Me substitution at the odd-numbered centers partly shifts the π-spin population from the seven- to the five-membered ring, whereas a shift in the opposite direction takes place on such a substitution at the even-numbered centers.*

The additivity of the substituent effects on the $|a_{H\mu}|$ values fails for $\mathbf{8}^{-\cdot}$ and $\mathbf{11}^{-\cdot}$, in which both odd- (μ = 1 and 3) and even-numbered centers (μ = 4, 6, and 8 or 2, 4, 6, and 8) bear alkyl groups. In these heavily substituted radical anions, there is a substantial interaction between the perturbations at the two sets of centers μ and individual contributions can hardly be singled out. The effect of the substitution at 4, 6, and 8 seems generally to prevail, at least for the seven-membered ring. The $|a_{H1,3}|$ value is throughout increased on Me substitution, presumably for reasons stated above in regard to the five-membered ring. Remarkably low values $|a_{H2}|$ are observed for the α-protons in $\mathbf{8}^{-\cdot}$–$\mathbf{10}^{-\cdot}$ and strikingly high ones $|a_{H5,7}|$ for such protons in $\mathbf{8}^{-\cdot}$–$\mathbf{11}^{-\cdot}$. As may be expected, replacement of a Me substituent at μ = 6 in $\mathbf{8}^{-\cdot}$ by a Pr and a *t*-Bu group in $\mathbf{9}^{-\cdot}$ and $\mathbf{10}^{-\cdot}$, respectively, does not lead to substantial changes in the coupling constants $a_{H\mu}$ other than those at the center 6 and its effect attenuates with the distance from this center.

For π-radical anions of many aromatic hydrocarbons, an excellent correlation has been found between the α-proton-coupling constants $|a_{H\mu}|$ and the squared coefficients $c_{j\mu}^2$ in the LUMO ψ_j, as calculated by the *Hückel* method [13c]. In the special case of $\mathbf{1}^{-\cdot}$, the correlation does not work equally well; the linear dependence of $|a_{H\mu}|$ on $c^2_{6\mu}$ seems to be affected by the different size of the two rings [4] and by an efficient π,π-spin polarization which is not accounted for by the simple theory [13a]. It is, therefore, unlikely that slight perturbations of the π-spin distribution, such as those brought about by alkyl substitutions, would all be faithfully reflected by conventional modifications of the *Hückel* model. A change in the $c^2_{6\mu}$ values of **1** as an effect of alkyl substitutions can be simulated by adding the term $h\beta$ to the *Coulomb* potential of the perturbed centers μ in **2**–**11**, wherein the parameter h accounts for the 'inductive effect' of the alkyl substituent [14a]. Alternatively, a second-order perturbation treatment can be applied to the $c^2_{6\mu}$ values of **1**, in which these values are modified with the use of h and the partial atom-atom polarizabilities for ψ_6 [14b] (see also [15]). Both procedures yield practically the same results for $c^2_{6\mu}$ of **2**–**11** provided that the absolute value of h is not too large (*e.g.*, an appropriate parameter h is -0.3 [15]). The changes in $c^2_{6\mu}$ of **2**–**11** relative to **1** conform to the trends in the observed hyperfine data $|a_{H\mu}|$ for the values at the seven-membered ring when the substitutions occur at even-numbered centers μ. Agreement between theory and experiment is less satisfactory for the values at the five-membered ring, in particular, when odd-numbered centers μ are substituted. This result is not unexpected, considering the pecularities of the $|a_{H\mu}|$ values at the five-membered ring (see above) and the negative π-spin populations ρ_μ at the odd-numbered centers μ.

Concluding Remark. – Some 50 years ago, *Plattner* has observed that Me substituents at the *odd*-numbered centers μ shift the long-wave band of **1** *bathochromically*, while those at the *even*-numbered ones have a *hypsochromic* effect on it [16]. These so-called *Plattner*'s rules [1] are readily rationalized in terms of the inductive first-order perturbation by the substituent as formulated by $(c^2_{6\mu} - c^2_{5\mu})h\beta$ for the LUMO (ψ_6) ← HOMO (ψ_5) transition [1a]. The relation of large $c^2_{6\mu}$ values for $\mu = 2, 4, 6$, and 8 *vs.* small ones for $\mu = 1, 3, 5$, and 7 is inverted in the case of $c^2_{5\mu}$. The findings reported here for the effect of alkyl substitution on the coupling constants $a_{H\mu}$ for $\mathbf{1}^{-\bullet}$ may, thus, be regarded, as somewhat akin to the *Plattner*'s rules.

Appendix. – Replacement of K^+ by Bu_4N^+ as the counterion without changing the solvent (DME) or the temperature (193 K) increases slightly the $|a_{H\mu}|$ values at the seven-membered ring and causes, in most cases, a very small decrease of such values at the five-membered ring. An effect of this kind points to a tightening of association with the counterion, because a similar finding has been reported for $\mathbf{1}^{-\bullet}$ when the cation-solvating power of the medium was lowered by using DME instead of DMF as the solvent [5b][7] or by raising the temperature [5]. Thus, there is an indication that Bu_4N^+ associates with $\mathbf{1}^{-\bullet}$–$\mathbf{11}^{-\bullet}$ in DME somewhat more strongly than K^+ which can be complexated by the solvent in a chelate-like fashion.

On the other hand, it should be noted that the hyperfine data given in *Table 1* for $\mathbf{3}^{-\bullet}$, $\mathbf{4}^{-\bullet}$, $\mathbf{6}^{-\bullet}$, and $\mathbf{8}^{-\bullet}$–$\mathbf{10}^{-\bullet}$ with K^+ as the counterion do not account for every detail of the ESR spectra. Inspection of the corresponding ENDOR spectra reveals that the signals pertinent to the three largest coupling constants are flanked by satellites appearing at the outer side for a_{H6} and $a_{H4,8}$ and at the inner one for a_{H2}. These satellites, due to a second species present in low concentration, evidently have the $|a_{H\mu}|$ values increased at the seven-membered ring ($\mu = 4, 6$, and 8) but decreased at the five-membered one ($\mu = 2$). The identification of the species in question as the radical anions more strongly associated with K^+ than those prevailing in DME at 193 K is corroborated by the finding that the satellites are no longer observed if the polar solvent *N,N,N*', *N*',*N*'',*N*''-hexamethylphosphoric triamide is added to DME prior to reaction with the metal.

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