

138. The Radical Ions of Dipleiadiene (Dicyclohepta[*de,ij*]naphthalene) and Its 12b,12c-Homo Derivative. An ESR and ENDOR Study

by Rainer Bachmann, Fabian Gerson*, and Pascal Merstetter

Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

and Emanuel Vogel

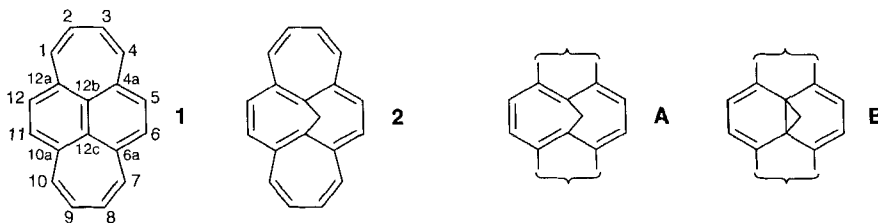
Institut für Organische Chemie der Universität zu Köln, Greinstrasse 4, D-50949 Köln 41

Dedicated to *Edgar Heilbronner* on the occasion of his 75th birthday

(24. V. 96)

The radical anions and the radical cations of dipleiadiene (dicyclohepta[*de,ij*]naphthalene; **1**) and its 12b,12c-homo derivative **2** were characterized by ESR and ENDOR spectroscopy. Their singly occupied orbitals are related to the degenerate nonbonding MOs of a 16-membered π -perimeter. The π -spin distribution over the perimeter is similar in the radical cations $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$, and an analogous statement holds for the radical anions $\mathbf{1}^{-\cdot}$ and $\mathbf{2}^{-\cdot}$. However, deviations of the π -system from planarity lead to a decrease in the absolute values of the negative coupling constants of the perimeter protons in $\mathbf{2}^{+\cdot}$ and $\mathbf{2}^{-\cdot}$ relative to those in $\mathbf{1}^{+\cdot}$ and $\mathbf{1}^{-\cdot}$. The hyperfine data for the perimeter protons in the radical ions correlate with the changes in ^{13}C chemical shifts on passing from the neutral compounds to the corresponding diions. It is concluded from the coupling constants of the CH_2 protons in the radical ions of **2** that the cation $\mathbf{2}^{+\cdot}$ exists in the methano-bridged form (A) of the neutral **2** (and, presumably, also of the dication $\mathbf{2}^{2+}$), whereas the anion $\mathbf{2}^{-\cdot}$ adopts the bisnorcaradiene form (B) of the dianion $\mathbf{2}^{2-}$.

Introduction. – The synthesis of dipleiadiene (dicyclohepta[*de,ij*]naphthalene; **1**) was reported several years ago [1]. According to the ^1H - and ^{13}C -NMR spectra of **1** [1] [2], the 16-membered π -perimeter of this nonalternant hydrocarbon is paratropic, and its π -system can be regarded as an annulene perturbed by the central $\text{C}=\text{C}$ bond. The 12b,12c-homo derivative **2** of **1** was synthesized in the same laboratory [3]. The paratropy of the 16-membered π -perimeter is retained in **2**, albeit it is attenuated relative to that in **1** [3], due to deviations of **2** from planarity [4]. Oxidation of **1** in $\text{SbF}_5/\text{SO}_2\text{ClF}$ 1:2 at 195 K yielded the dication $\mathbf{1}^{2+}$ [2], while both dianions $\mathbf{1}^{2-}$ [2] and $\mathbf{2}^{2-}$ [3] were prepared by reduction of the corresponding neutral compounds **1** and **2** with K in THF at ambient temperature. The 16-membered π -perimeter in all three diions becomes diatropic [2] [3], following the removal ($\mathbf{1}^{2+}$) or the uptake ($\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$) of two electrons. Moreover, the NMR data for $\mathbf{2}^{2-}$ indicate that the dianion favors the ‘closed’ bisnorcaradiene form **B** over the ‘open’, methano-bridged form **A** found for the neutral **2** [3].



Here, we describe the ESR and ENDOR spectra of the radical cations $1^{+\cdot}$ and $2^{+\cdot}$, and the radical anions $1^{-\cdot}$ and $2^{-\cdot}$. Either form, **A** or **B**, is considered for $2^{+\cdot}$ and $2^{-\cdot}$.

Results. – Starting from the neutrals **1** and **2**, the radical cations $1^{+\cdot}$ and $2^{+\cdot}$ were generated with AlCl_3 or tris(*p*-bromophenyl)ammoniumyl hexachloroantimonate in CH_2Cl_2 at room temperature, while the corresponding radical anions, $1^{-\cdot}$ and $2^{-\cdot}$, were produced with K in 1,2-dimethoxyethane (DME) at 195 K. In the case of $2^{-\cdot}$, addition of *N,N,N',N',N'',N''*-hexamethylphosphoric triamide (HMPT) to DME (1:10) was required to slow down the further reduction to the dianion 2^{2-} . The ESR and ENDOR spectra of the four radical ions, $1^{+\cdot}$, $2^{+\cdot}$, $1^{-\cdot}$, and $2^{-\cdot}$, were taken between 243 and 193 K, in which range they do not markedly depend on the temperature. *Figs. 1–4* show these spectra for each of the radical ions. The coupling constants, $a_{\text{H}\mu}$, of the three sets of four equivalent perimeter protons in $1^{+\cdot}$, $2^{+\cdot}$, $1^{-\cdot}$, and $2^{-\cdot}$, as well as those, $a_{\text{H}}(\text{CH}_2)$, of the pair of protons in the central fragment of $2^{+\cdot}$ and $2^{-\cdot}$ were determined from the positions of the ENDOR signals and certified by simulation of the ESR spectra; they are listed in the *Table*. Assignments of the $a_{\text{H}\mu}$ values to protons at individual C-centers $\mu = 1$ –12 are justified in the *Discussion*¹⁾. General-TRIPLE-resonance experiments carried out on the ENDOR signals [5] indicated that all coupling constants (with the possible exception of that with the smallest absolute value, 0.011 mT, for $2^{-\cdot}$) have the same sign which should be

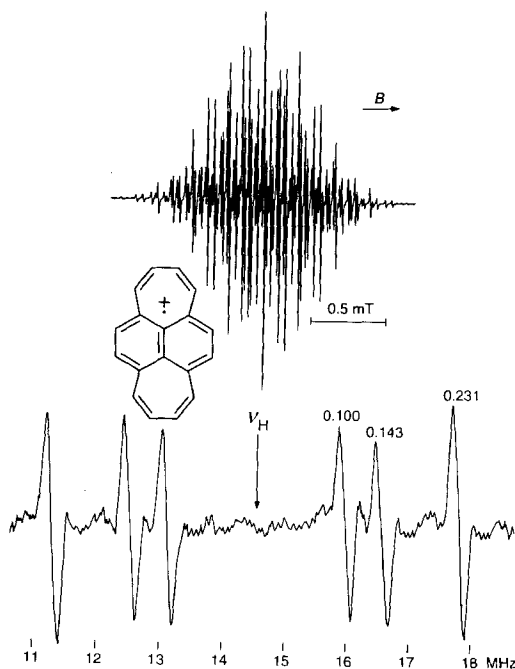


Fig. 1. Top: ESR spectrum of $1^{+\cdot}$ (solvent CH_2Cl_2 , counterion $[\text{AlCl}_3-\text{CH}_2\text{Cl}_2]^-$, temp. 198 K). Bottom: ^1H -ENDOR spectrum of $1^{+\cdot}$ (taken under the same conditions). The numbers above the signals are the absolute values of the coupling constants in mT.

¹⁾ For the sake of comparison, the numbering of the C-atoms in **1** was also used for **2**.

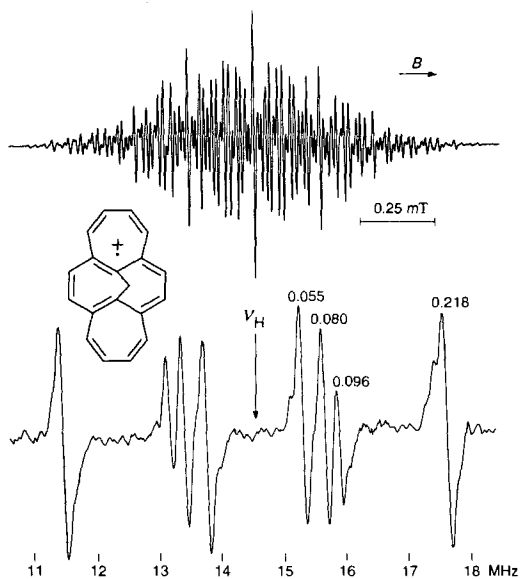


Fig. 2. Top: ESR spectrum of $2^{+\cdot}$ (solvent CH_2Cl_2 , counterion SbCl_6^- , temp. 198 K). Bottom: ^1H -ENDOR spectrum of $2^{+\cdot}$ (taken under the same conditions). The numbers above the signals are the absolute values of the coupling constants in mT. $2^{+\cdot}$ is drawn in the methano-bridged form A (see Discussion).

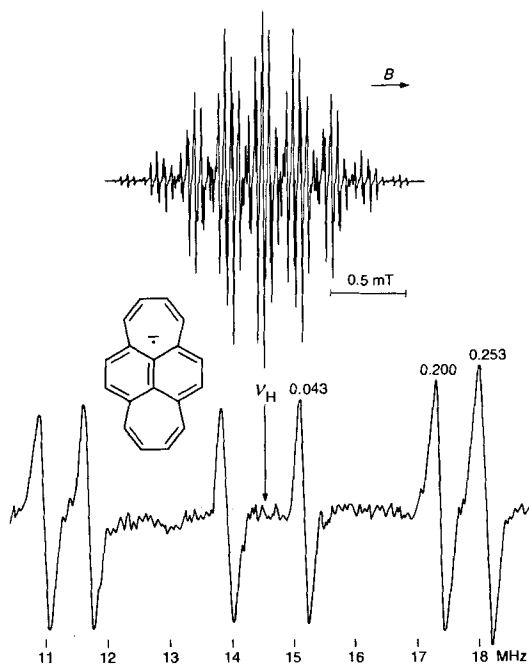


Fig. 3. Top: ESR spectrum of $1^{\cdot-}$ (solvent DME, counterion K^+ , temp. 198 K). Bottom: ^1H -ENDOR spectrum of $1^{\cdot-}$ (taken under the same conditions). The numbers above the signals are the absolute values of the coupling constants in mT.

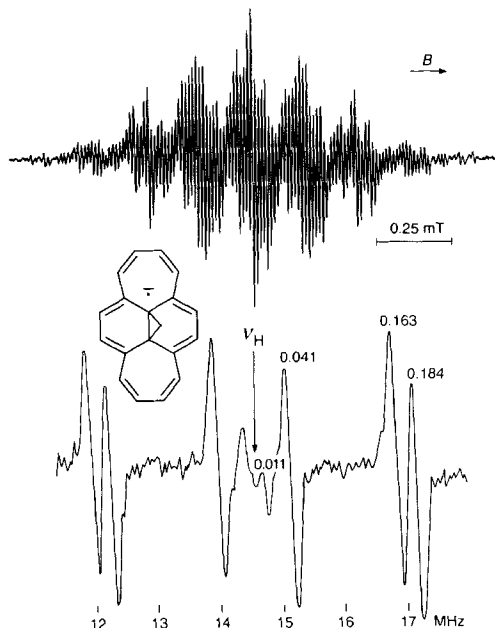


Fig. 4. Top: ESR spectrum of $\mathbf{2}^{\bullet-}$ (solvent DME/HMPT, 10:1, counterion K^+ , temp. 198 K). Bottom: ^1H -ENDOR spectrum of $\mathbf{2}^{\bullet-}$ (taken under the same conditions). The numbers above the signals are the absolute values of the coupling constants in mT. $\mathbf{2}^{\bullet-}$ is drawn in the bisnorcaradiene form **B** (see Discussion).

Table. ^1H -Coupling Constants $a_{\text{H}\mu}$ and $a_{\text{H}}(\text{CH}_2)$ [mT] for the Radical Ions $\mathbf{1}^{\bullet+}$, $\mathbf{2}^{\bullet+}$, $\mathbf{1}^{\bullet-}$, and $\mathbf{2}^{\bullet-}$ and Changes, $\Delta\delta_{\text{C}\mu}^+$ and $\Delta\delta_{\text{C}\mu}^-$, in ^{13}C Chemical Shifts^{a)}, on Passing from the Neutrals **1** and **2** to the Dions $\mathbf{1}^{2+}$, $\mathbf{1}^{2-}$, and $\mathbf{2}^{2-}$

	μ			
	1, 4, 7, 10	2, 3, 8, 9	5, 6, 11, 12	
$a_{\text{H}\mu}(\mathbf{1}^{\bullet+})$	-0.100	-0.231	-0.143	
$\Delta\delta_{\text{C}\mu}^+ = \delta_{\text{C}\mu}(\mathbf{1}^{2+}) - \delta_{\text{C}\mu}(\mathbf{1})$	+15.6 ^{b)}	+24.8 ^{b)}	+18.4 ^{b)}	
$a_{\text{H}\mu}(\mathbf{2}^{\bullet+})$	-0.055 ^{c)}	-0.218	-0.080 ^{c)}	
	^{d)}	^{d)}	^{d)}	
$a_{\text{H}}(\text{CH}_2; \mathbf{2}^{\bullet+})$				-0.096
$a_{\text{H}\mu}(\mathbf{1}^{\bullet-})$	-0.253	-0.200	-0.043	
$\Delta\delta_{\text{C}\mu}^- = \delta_{\text{C}\mu}(\mathbf{1}^{2-}) - \delta_{\text{C}\mu}(\mathbf{1})$	-40.8	-22.7	-10.0	
$a_{\text{H}\mu}(\mathbf{2}^{\bullet-})$	-0.163	-0.184	-0.041	
$\Delta\delta_{\text{C}\mu}^- = \delta_{\text{C}\mu}(\mathbf{2}^{2-}) - \delta_{\text{C}\mu}(\mathbf{2})$	-26.9	-28.0	-23.9	
$a_{\text{H}}(\text{CH}_2; \mathbf{2}^{\bullet-})$				0.011 ^{e)}

^{a)} Experimental error: ± 0.001 mT in $a_{\text{H}\mu}$ and ± 0.1 in $\delta_{\text{C}\mu}$. ^{b)} Include susceptibility corrections for the $\delta_{\text{C}\mu}(\mathbf{1}^{2+})$ values measured with an external reference [2]. ^{c)} Assignment uncertain. ^{d)} $\delta_{\text{C}\mu}(\mathbf{2}^{2+})$ values not available. ^{e)} Sign not derived experimentally.

negative according to the theory for the α -protons²⁾ [6]. The g factor for both $\mathbf{1}^{\bullet+}$ and $\mathbf{1}^{\bullet-}$ is 2.0027, while those of $\mathbf{2}^{\bullet+}$ and $\mathbf{2}^{\bullet-}$ are 2.0026 and 2.0028, respectively (experimental error: ± 0.0001).

²⁾ In ESR spectroscopy, protons separated by 0,1,2, ... sp^3 -hybridized C-atoms from the nearest π -center are denoted $\alpha, \beta, \gamma, \dots$. Accordingly, the protons at the centers $\mu = 1-12$ of the 16-membered π -perimeter in **1** and **2** are α , while the CH_2 protons in **2** are β in the methano bridge of the form **A** but γ in the cyclopropanediylidene fragment of the form **B**.

Discussion. – *Diplediadiene* (**1**). The frontier orbitals, $\psi_{AA}(a_u)$ and $\psi_{SS}(b_{1u})$, of the essentially planar **1** [1] [2], which are depicted diagrammatically in Fig. 5, can be derived from the nonbonding degenerate MOs of the 16-membered π -perimeter. The subscripts S and A stand for symmetric and antisymmetric with respect to the vertical mirror planes xz and yz , while a_u and b_{1u} refer to the irreducible representations in the symmetry group D_{2h} of **1**. Whereas in ψ_{AA} the π -perimeter does not interact with the π -system of the central C=C bond, and its nonbonding level is retained ($E_{AA} = \alpha$ in the Hückel model), it does so in ψ_{SS} which becomes antibonding ($E_{SS} = \alpha - 0.29\beta$; Fig. 5). The HOMO and LUMO of **1** are thus properly described by ψ_{AA} and ψ_{SS} , respectively. The single occupancy of ψ_{AA} in the radical cation **1**⁺ implies a uniform π -spin distribution over the 16-membered perimeter with the π -spin population $\rho_\mu = 1/16 = 0.0625$ at each center $\mu = 1-12$, a value which is only marginally modified by the *McLachlan* procedure [7]. Use of *McConnell* equation for α -protons, $a_{H\mu} = Q \cdot \rho_\mu$ [8], with the proportionality factor $Q = -2.5$ mT yields the average of the coupling constants $a_{H\mu}$, -0.231 , -0.143 , and -0.100 mT, observed for the three sets of four equivalent perimeter protons in **1**⁺. Assignments of these hyperfine data, $a_{H\mu}$, to the α -protons at the individual perimeter centers μ (Table) are based on comparison with the changes in the ¹³C chemical shifts, $\Delta\delta_{C\mu}^+ = \delta_{C\mu}(\mathbf{1}^{2+}) - \delta_{C\mu}(\mathbf{1})$, on passing from the neutral **1** [1] to the dication **1**²⁺ [2]. Such a procedure is justified by the experience that the $\delta_{C\mu}$ values reflect the π -charge populations at the C-centers μ [9] and, therefore, the differences $\Delta\delta_{C\mu}^+$ are roughly proportional to the squared LCAO coefficients, c_μ^2 , of the HOMO, as are the α -proton coupling constants, $a_{H\mu}$, for **1**⁺, in virtue of the π -spin populations ρ_μ [10].

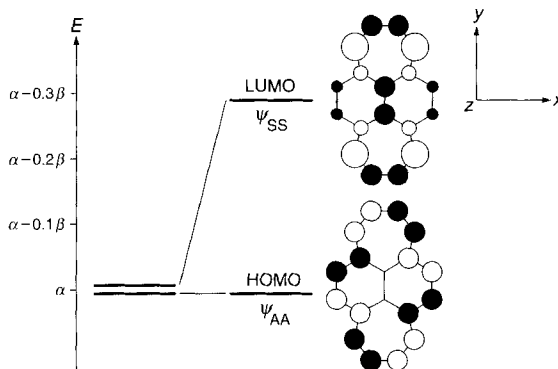


Fig. 5. Frontier orbitals, ψ_{SS} and ψ_{AA} , of **1** as derived from the degenerate nonbonding MOs of the 16-membered π -perimeter

In contrast to the single occupancy of ψ_{AA} in **1**⁺, such an occupancy of ψ_{SS} in the radical anion **1**⁻ does not presuppose a uniform π -spin distribution over the centers μ of the 16-membered perimeter (Fig. 5). Thus, assignments of the coupling constants $a_{H\mu}$, -0.253 , -0.200 , and -0.043 mT, to the three sets of four α -protons in **1**⁻ (Table) could be made by correlation with the π -spin populations ρ_μ calculated by the *McLachlan* procedure. Moreover, using the arguments presented above for the comparison of the $a_{H\mu}$ values for **1**⁺ with the differences $\Delta\delta_{C\mu}^+$ for **1** and **1**²⁺, one anticipates an analogous

parallelism between the coupling constants $a_{\text{H}\mu}$ for $\mathbf{1}^{\cdot-}$ and the changes in the ^{13}C chemical shifts, $\Delta\delta_{\text{C}\mu}^- = \delta_{\text{C}\mu}(\mathbf{1}^{2-}) - \delta_{\text{C}\mu}(\mathbf{1})$, on passing from the neutral $\mathbf{1}$ [1] to the dianion $\mathbf{1}^{2-}$ [2], because both sets of data should depend on the squared LCAO coefficients, c_{μ}^2 , of the LUMO. Gratifyingly, the assignments indicated by such a relation between the ESR and NMR data agree with those based on the calculated π -spin populations ρ_{μ} .

Homodiplediadiene 2. For the following reasons, interpretation of the ^1H -hyperfine data gave more problems for the radical ions $\mathbf{2}^+$ and $\mathbf{2}^{\cdot-}$ than for $\mathbf{1}^+$ and $\mathbf{1}^{\cdot-}$. *i)* As stated in the *Introduction*, the neutral $\mathbf{2}$ exists in the methano-bridged form **A**, whereas the dianion $\mathbf{2}^{2-}$ favors the bisnorcaradiene form **B**, so that both forms must be considered for $\mathbf{2}^+$ and $\mathbf{2}^{\cdot-}$. *ii)* The marked deviations from planarity in $\mathbf{2}$ [4] should carry over to $\mathbf{2}^+$ and $\mathbf{2}^{\cdot-}$ in either form **A** or **B**. *iii)* The dication $\mathbf{2}^{2+}$ has not been prepared.

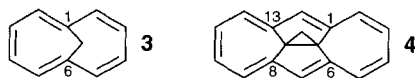
Irrespective of the form **A** or **B** and despite the nonplanarity, the frontier orbitals of $\mathbf{2}$, $\psi_{\text{AA}}(a_2)$ and $\psi_{\text{SS}}(a_1)$, can also be traced back to the nonbonding MOs of the 16-membered π -perimeter, in a way analogous to that followed for $\mathbf{1}$; the notation a_2 and a_1 now refers to the symmetry group C_{2v} of $\mathbf{2}$. Again in ψ_{AA} , the π -perimeter does not interact with appropriate orbitals of the central fragment, which is either $>\text{C}-\text{CH}_2-\text{C}<$ in **A** or $-\text{C}-\text{CH}_2-\text{C}-$ in **B**, and ψ_{AA} remains essentially nonbonding. In contrast, the energy of ψ_{SS} is raised by such an interaction to an antibonding level. As far as the perimeter is concerned, the HOMO $\psi_{\text{AA}}(a_2)$ and the LUMO $\psi_{\text{SS}}(a_1)$ of $\mathbf{2}$ should thus closely resemble the corresponding MOs $\psi_{\text{AA}}(a_u)$ and $\psi_{\text{SS}}(b_{1u})$ of $\mathbf{1}$ (*Fig. 5*). The single occupancy of the relevant frontier orbital in the radical ion means that the π -spin distribution over the centers μ of the perimeter in $\mathbf{2}^+$ and $\mathbf{2}^{\cdot-}$ should be similar to that in $\mathbf{1}^+$ and $\mathbf{1}^{\cdot-}$, respectively. The coupling constants, $a_{\text{H}\mu}$, of the perimeter α -protons in $\mathbf{2}^+$ are, therefore, expected to be comparable to the corresponding values for $\mathbf{1}^+$, and the same statement holds for $\mathbf{2}^{\cdot-}$ and $\mathbf{1}^{\cdot-}$. Such an expectation is, in fact, borne out by experimental data (*Figs. 1–4* and *Table*), although some absolute values $|a_{\text{H}\mu}|$ for $\mathbf{2}^+$ and $\mathbf{2}^{\cdot-}$ are markedly reduced relative to those for $\mathbf{1}^+$ and $\mathbf{1}^{\cdot-}$, the sums of $|a_{\text{H}\mu}|$ for the α -protons at all 12 centers μ of the perimeter being 1.41 ($\mathbf{2}^+$) vs. 1.90 mT ($\mathbf{1}^+$) and 1.55 ($\mathbf{2}^{\cdot-}$) vs. 1.98 mT ($\mathbf{1}^{\cdot-}$). This decrease is a consequence of deviations of $\mathbf{2}^+$ and $\mathbf{2}^{\cdot-}$ from planarity, as the coupling constants of the α -protons in nonplanar π -radicals are affected by positive contributions arising from π, σ -spin delocalization which partially compensate the negative ones due to π, σ -spin polarization governing such coupling constants in planar π -radicals [11] [12].

Assignments of the coupling constants $a_{\text{H}\mu}$ to the three sets of four equivalent perimeter α -protons in $\mathbf{2}^+$ and $\mathbf{2}^{\cdot-}$ could thus be guided by analogy with $\mathbf{1}^+$ and $\mathbf{1}^{\cdot-}$. This procedure is particularly straightforward for those coupling constants which seem least affected by nonplanarity of $\mathbf{2}^+$ and $\mathbf{2}^{\cdot-}$, namely the one with the distinctly largest $|a_{\text{H}\mu}|$ value for the radical cation, -0.218 ($\mathbf{2}^+$) vs. -0.231 mT ($\mathbf{1}^+$), and the other with the by far smallest $|a_{\text{H}\mu}|$ value for the radical anion, -0.041 ($\mathbf{2}^{\cdot-}$) vs. -0.043 mT ($\mathbf{1}^{\cdot-}$). It is, therefore, logical to assign these coupling constants, $a_{\text{H}\mu}$, to the α -protons at the same perimeter centers μ in $\mathbf{2}^+$ and $\mathbf{2}^{\cdot-}$ as in $\mathbf{1}^+$ and $\mathbf{1}^{\cdot-}$, respectively (*Table*). More problematic are the assignments of the two remaining, less conspicuous $a_{\text{H}\mu}$ values to sets of four α -protons in $\mathbf{2}^+$ and $\mathbf{2}^{\cdot-}$, in view of the larger differences with their counterparts in $\mathbf{1}^+$ and $\mathbf{1}^{\cdot-}$. For $\mathbf{2}^{\cdot-}$, comparison of these values with the changes, $\Delta\delta_{\text{C}\mu}^- = \delta_{\text{C}\mu}(\mathbf{2}^{2-}) - \delta_{\text{C}\mu}(\mathbf{2})$, on passing from the neutral $\mathbf{2}$ to the dianion $\mathbf{2}^{2-}$ [3], not only confirms the assignment of -0.041 mT, but it also suggests those of the two coupling constants with the larger $|a_{\text{H}\mu}|$ values, -0.184 and -0.163 mT (*Table*). In the case of $\mathbf{2}^+$, an analogous comparison of the coupling

constants $a_{\text{H}\mu}$ with the changes in the ^{13}C chemical shifts, $\Delta\delta_{\text{C}\mu}^+ = \delta_{\text{C}\mu}(\mathbf{2}^{2+}) - \delta_{\text{C}\mu}(\mathbf{2})$, is not practicable, because the pertinent NMR data for the dication $\mathbf{2}^{2+}$ are not available. *McLachlan* and AM1 [13] calculations of $\mathbf{2}^{2+}$ in both forms **A** and **B** clearly support the assignment of -0.218 mT, yet those of the remaining two coupling constants with the smaller $|a_{\text{H}\mu}|$ values, -0.080 and -0.055 mT, remain rather uncertain (*Table*).

In contrast to the $a_{\text{H}\mu}$ values of the *three sets of four* perimeter α -protons, the coupling constants $a_{\text{H}}(\text{CH}_2)$ observed for the *single pair* of equivalent protons in the central fragment of $\mathbf{2}^{2+}$ and $\mathbf{2}^{2-}$ could be directly and unequivocally assigned. Whereas the former hardly provide any information of the actual form **A** or **B**, the latter are highly relevant to such a structural feature. This is because the two CH_2 protons are β in the **A** form but γ in **B**³⁾, and the coupling constants of the β - and γ -protons usually differ by an order of magnitude in their absolute values [6]. Moreover, the sign of the coupling constant of β -protons is generally the same as that of the π -spin population ρ_{μ} at the substituted center μ , while that of the γ -protons varies somehow with the nature of the substituent. The identification of the CH_2 protons with β or γ can thus be achieved by considering the absolute value and the sign of their coupling constant, combined with the use of MO calculations such as the *McLachlan* procedure and AM1.

For $\mathbf{2}^{2+}$, the substantial absolute value and the negative sign of $a_{\text{H}}(\text{CH}_2)$ (*Table*) are fully consistent with those expected for the β -protons in the form **A**, because, with the single occupancy of $\psi_{\text{AA}}(a_2)$ in $\mathbf{2}^{2+}$, negative π -spin populations ρ_{μ} of *ca.* -0.03 are predicted at the bridged centers $\mu = 12\text{b}$ and 12c in that form⁴⁾. The value of -0.096 mT compares favorably with -0.115 mT for the β -protons of the CH_2 bridge in the radical anion of 1,6-methano[10]annulene (**3**) [11]³⁾. Admittedly, the likewise negative π -spin populations ρ_{μ} at the bridged centers $\mu = 1$ and 6 in $\mathbf{3}^{2-}$ are markedly higher than the corresponding ρ_{μ} values for $\mathbf{2}^{2+}$, but hyperconjugation, which is responsible for the coupling to β -protons, is less efficient in radical anions than in radical cations. An alternative form **B** can be excluded for $\mathbf{2}^{2+}$, because, with the single occupancy of $\psi_{\text{AA}}(a_2)$, the coupling constant $a_{\text{H}}(\text{CH}_2)$ of the γ -protons should be negligibly small.



On the other hand, the small absolute value of $a_{\text{H}}(\text{CH}_2)$ in $\mathbf{2}^{2-}$ (*Table*) is appropriate for the γ -protons in the form **B** with the single occupancy of $\psi_{\text{SS}}(a_2)$, whereas, according to calculations, such an occupancy in the form **A** would require an extremely large and positive β -proton coupling constant. The value of 0.011 mT is even smaller than 0.028 mT⁴⁾ for the CH_2 γ -protons in the radical anion of 1,6:8,13-cyclopropanediylidene[14]annulene (**4**) [12], in which the π -spin populations ρ_{μ} at the centers $\mu = 1, 6, 8,$ and 13 , proximate to the three-membered ring, are similar in magnitude to those at the corresponding centers $\mu = 4\text{a}, 6\text{a}, 10\text{a},$ and 12a in $\mathbf{2}^{2-}$.

The coupling constants $a_{\text{H}}(\text{CH}_2)$ thus indicate that the radical cation $\mathbf{2}^{2+}$ must exist in the methano-bridged form **A** of the neutral **2**, whereas the radical anion $\mathbf{2}^{2-}$ ought to adopt the bisnorcaradiene form **B** of the dianion $\mathbf{2}^{2-}$. The ease of conversion of $\mathbf{2}^{2-}$ to $\mathbf{2}^{2-}$

³⁾ The negative sign of -0.115 mT was derived later on by general-TRIPLE-resonance spectroscopy.

⁴⁾ The sign of 0.011 and 0.028 mT was not determined experimentally.

upon reduction, particularly in nonpolar solvents, is also consistent with the similar structure of the two species, a finding characteristic of the radical anion and dianion of cyclooctatetraene [14] which are both planar unlike the neutral compound. AM1 Calculations point to a single minimum at the energy hypersurface of both diions $\mathbf{2}^{2+}$ and $\mathbf{2}^{2-}$. For the latter, such a minimum occurs for the form **B**, in accord with experiment, while, for the former, it is due to the form **A**. Therefore, one concludes that in the redox sequence represented by the dication $\mathbf{2}^{2+}$, the radical cation $\mathbf{2}^{+\cdot}$, the neutral **2**, the radical anion $\mathbf{2}^{\cdot-}$, and the dianion $\mathbf{2}^{2-}$, the transition from the methano-bridged form **A** to the bisnorcaradiene form **B** takes place on passing from **2** to $\mathbf{2}^{\cdot-}$.

Experimental. – The syntheses of **1** [1] [2] and **2** [3] are described elsewhere. The ESR spectra were taken on a *Varian-E9* instrument, whereas a *Bruker-ESP-300* system served for the ENDOR and TRIPLE-resonance studies.

This work was supported by the *Swiss National Science Foundation*.

REFERENCES

- [1] E. Vogel, B. Neumann, W. Klug, H. Schmickler, J. Lex, *Angew. Chem. Int. Ed.* **1985**, *24*, 1046.
- [2] J. Werner, Dissertation, Köln, 1988.
- [3] C. Ritz, Dissertation, Köln, 1991.
- [4] R. Arnz, Dissertation, Köln, 1989.
- [5] H. Kurreck, B. Kirste, W. Lubitz, 'Electron Nuclear Double Resonance Spectroscopy of Radicals in Solutions', VCH Publishers, New York, 1989, Chapt. 2.
- [6] F. Gerson, 'High-Resolution ESR Spectroscopy', Wiley and Verlag-Chemie, New York and Weinheim, 1970, Chapt. 1.5.
- [7] A. D. McLachlan, *Mol. Phys.* **1960**, *3*, 233.
- [8] H. M. McConnell, *J. Chem. Phys.* **1956**, *24*, 632.
- [9] J. W. Emsley, J. Feeney, L. H. Sutcliffe, 'High Resolution NMR Spectroscopy', Pergamon Press, Oxford, 1966, Vol. 2, Chapt. 12.2; D. H. O'Brien, A. J. Hart, C. R. Russell, *J. Am. Chem. Soc.* **1975**, *97*, 4410. R. N. Young, *Prog. NMR Spectrosc.* **1979**, *12*, 261.
- [10] K. Müllen, *Chem. Rev.* **1984**, *84*, 603.
- [11] F. Gerson, E. Heilbronner, W. A. Böll, E. Vogel, *Helv. Chim. Acta* **1965**, *48*, 1494; F. Gerson, K. Müllen, E. Vogel, *ibid.* **1971**, *54*, 2731.
- [12] F. Gerson, K. Müllen, E. Vogel, *J. Am. Chem. Soc.* **1972**, *94*, 2924; F. Gerson, J. Knöbel, J. Lopez, E. Vogel, *Helv. Chim. Acta* **1985**, *68*, 371.
- [13] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902.
- [14] F. Gerson, W. B. Martin, jr., G. Plattner, F. Sondheimer, H. N. C. Wong, *Helv. Chim. Acta* **1976**, *59*, 2038.