261. The Radical Anions of Heptalene and 1,7-Methano-[12]annulene

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Summary. The radical anions of heptalene and of 1,7-methano-[12]annulene are generated by metal reduction and characterized by means of their ESR.-spectra. Whereas the neutral hydrocarbons are π-bond localized their corresponding radical anions turn out to be π-bond delocalized. This could be deduced from an interpretation of the different hyperfine splittings using a simple MO-model.

1. Introduction. – By means of ^{1}H- and ^{13}C-NMR.-spectroscopy we could show recently that both heptalene (**1**) and 1,7-methano-[12]annulene (**2**) are π-bond localized, but exhibit a fast and reversible π-bond shift [1] [2]. In contrast to the neutral compounds the corresponding dianions – as could be demonstrated by UV.- and NMR.-spectroscopy – have their π-bonds delocalized [3] [4]. Since we prepared the dianions by alkali-metal reduction we were also able to detect the intermediate radical anions (see Fig. 1); their ESR.-spectra are described here. A closer spectroscopical study of the radical anions and dianions obtained by electrochemical reduction will be published elsewhere [5].

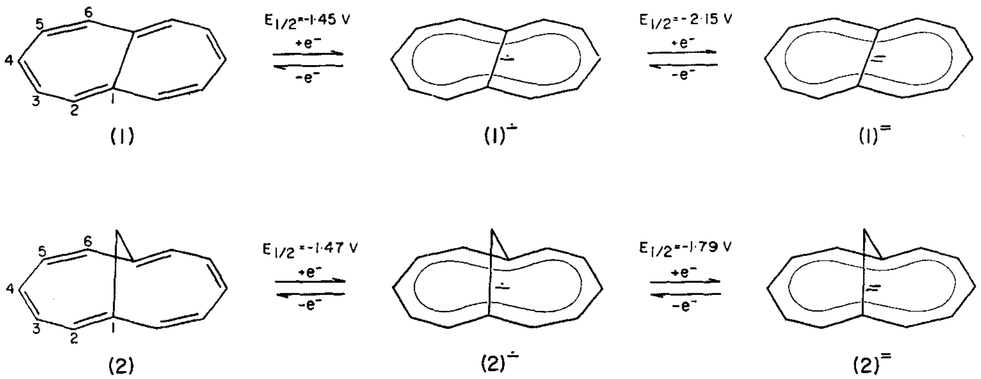

Fig. 1. *The reduction of heptalene and 1,7-methano-[12]annulene to their corresponding radical anions and dianions* (the reported half-wave potentials have been measured *versus* a calomel reference electrode, 1N KCl)

Discussing the bonding situation in the radical anions of heptalene ($\mathbf{1}^{\dot{-}}$) and 1,7-methano-[12]annulene ($\mathbf{2}^{\dot{-}}$) one is faced with the problem of deciding, whether these $4n+1$-π-systems are π-bond delocalized or localized. One can consider both **1** and **2** to a first approximation as a 12π-perimeter system perturbed by a CH_2-bridge in the case of 1,7-methano-[12]annulene or by a central σ-bond in the case of heptalene. This simple but instructive point of view is in accordance with a perturbational MOtreatment of the alternant hydrocarbon [12]annulene [6]. Consequently, the lowest antibonding orbital which is occupied by the unpaired electron in the radical anion should originate from a perturbation of the degenerate non-bonding [12]annulene orbitals.

2. The ESR.-spectra of heptalene and 1,7-methano-[12]annulene radical anions. – Upon polarographic reduction both heptalene and 1,7-methano-[12]annulene are reversibly converted to their corresponding radical anions and dianions. The half-wave potentials of the reduction steps are reported in the preceeding publication [4] (see also Fig. 1). As will be discussed below, an eventual distinction between π-bond delocalized and π-bond localized structures based on the experimental hyperfine coupling constants requires ESR.-spectra with optimal spectral resolution. Regardless of the dipolar interaction, which can be reduced by progressive dilution, the resolution is also determined by the rate of electron exchange between the radical anion, the neutral molecule or/and the dianion. If one follows the alkali-metal reduction of heptalene [4] and of 1,7-methano-[12]annulene to their corresponding dianions by recording the ESR.- and NMR.-spectra after defined times of contact between the solution and the metal one can deduce the following results: despite a detectable radical concentration at the beginning of the heptalene reduction the high resolution of the ^{1}H-NMR.-spectrum is maintained [4]. In the analogous experiment with 1,7-methano-[12]annulene one observes some broadening of the lines from the beginning of the reaction. The line width obtained for the ESR.-spectrum of the heptalene radical anion is of the order of 40 mG, whereas in the spectrum of the 1,7-methano-[12]annulene radical anion it is *ca.* 600 mG and one resolves only 2 from the 4 possible coupling constants.

The line broadening at the beginning of the reduction is due to the electron exchange between the neutral molecule (which is present in large excess) and the radical anion. The rate of this exchange process has to be correlated with the relative position in energy of the lowest unoccupied MO in the neutral molecule and the MO occupied in the radical by the unpaired electron. This difference is probably smaller in the case of the bridged [12]annulene than in the case of heptalene, the geometries of R and $R^{\dot{-}}$ being more similar for the bridged [12]annulene than for heptalene.

Since the fast electron exchange between the neutral species and the radical anion of the bridged annulene causes a severe line broadening in the ESR.-spectrum (this is demonstrated in Fig. 2) we tried to generate the radical anion cleanly. This proved possible by electrolysis in a flow cell in which current and flow rate were

Table 1. *Experimental and calculated* (see text) *ESR. hyperfine coupling constants* (Gauss) *of the heptalene* ($\mathbf{1}^{\dot{-}}$) *and 1,7-methano-[12]annulene* ($\mathbf{2}^{\dot{-}}$) *radical anions*

		a = a (H-3,5,9,11)	a′ = a (H-2,6,8,12)	a″ = a (H-4,10)	a‴ = a (CH$_2$)
($\mathbf{1}^{\dot{-}}$)	(exp.)	– 5.35	+ 0.69	+ 0.79	
($\mathbf{1}^{\dot{-}}$)	(calc.)	– 5.49	+ 0.74	+ 1.46	
($\mathbf{2}^{\dot{-}}$)	(exp.)	– 3.64	+ 2.24	± 0.33[a]	± 0.19[a]
($\mathbf{2}^{\dot{-}}$)	(calc.)	– 5.67	+ 1.51	+ 1.52	

[a] Tentative assignment.

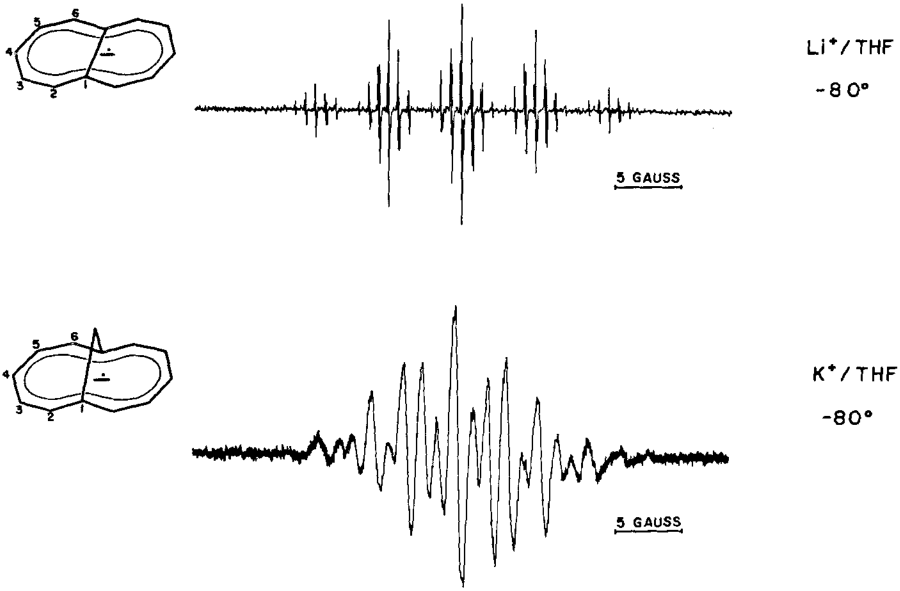

Fig. 2. *ESR.-spectra of* a) *heptalene* (lithium, tetrahydrofurane, – 80°), b) *1,7-methano-[12]annulene* (potassium, tetrahydrofurane, – 80°) *radical anions*

adjusted in order to obtain the transfer of exactly one electron per mol [7]. By passing the electrolyzed solution through the ESR.-cavity we obtained a spectrum with an experimental line width of 55 mG. This enabled us to resolve all coupling constants; their values are given in Table 1.

3. Interpretation of the ESR.-spectra. – The hyperfine coupling constants resulting from a spectral simulation [8] are reported in Table 1 together with their assignment and their calculated values (see below).

In addition to the use of a MO-model, there is a simple symmetry criterion which not only facilitates the assignment (groups of 2 and 4 protons, respectively) but also characterizes the bonding situation. Whereas π-bond delocalization imposes C_{2v} (D_{2h}, if the ring is expected to be planar) to the perimeter, a C_2-axis perpendicular to the ring and passing through the midpoint of the segment C(1)–C(7) would be the only element of symmetry in the localized situation. We would then expect 5 different coupling constants each corresponding to 2 protons. The parameters given in Table 1, namely the fact that only 3 coupling constants are observed for the ring protons, indicate the existence of two planes of symmetry. This demonstrates that – on the ESR. time scale (see below) – the radical anions $\mathbf{1}^{\dot{-}}$ and $\mathbf{2}^{\dot{-}}$ exist as π-bond delocalized species.

The lowest antibonding HMO in heptalene (all $\beta_{\mu\nu} = 1$) is schematically represented in Fig. 3. The existence of a nodal plane through the ring centers C(4) and C(10) and of a high spin density at position 3 provides an explanation for the experimental finding of one large (4H) and two small coupling constants (2H and 4H). The assignment of the large coupling a = –5.35 G to the protons on the centers

3, 5, 9 and 11 is thus beyond any doubt. The assignment of the two small couplings results immediately from the number of nuclei on each set. The calculation of these small coupling constants using only a HMO-model is not possible, unless one takes into account the π,π-polarization effect and uses the *McLachlan* formalism ($\lambda = 1.2$) [9]. With this approach one finds the values reported in Table 1 (the *McConnell* coefficient Q was taken as -25 G).

One should note here the general agreement found between the experimental and the calculated values of the small coupling constants a′ and a″. The calculation indicates that the small coupling constants must be positive. Furthermore one can deduce that the radical anion of heptalene is most likely planar.

The assignment of the different hyperfine splitting parameters in the case of the radical anion of 1,7-methano-[12]annulene ($\mathbf{2}^{\dot{-}}$) is not as straightforward as in the case of the radical anion of heptalene. Here we have two large couplings, each corresponding to a set of four protons, and two small couplings corresponding to a set of two protons.

To interprete the spin density distribution in the radical anion of 1,7-methano-[12]annulene ($\mathbf{2}^{\dot{-}}$) one can best start with the structure of an idealized [12]annulene of D_{12h}-symmetry. As it is to be seen from the schematic representation in Fig. 3 the two non-bonding HMO's in this situation are degenerate. To arrive at a more realistic model one has to impose the appropriate symmetry by a judicious choice of the individual resonance integrals or one has to take into account the effect of bridging by introducing a small value of β_{17}. Such a perturbation of the original D_{12h}-perimeter will, of course, lower the original symmetry. In a delocalized perimeter of D_{2h}-sym-

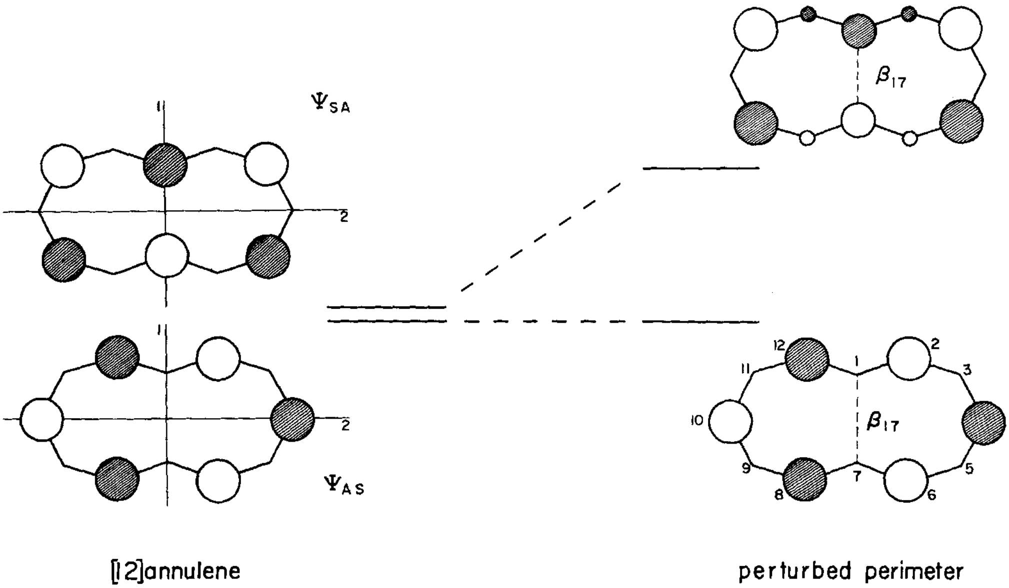

Fig. 3. *Schematic representation of the two non-bonding HMO's in [12]annulene and of the bridging effect.* The radii of the circles are proportional to the absolute values of the LCAO-coefficients; blank and dotted areas indicate the relative signs of these coefficients

metry (this is the symmetry imposed by the bridging) the degeneracy of the non-bonding orbitals is destroyed[1]). Introduction of a non-zero resonance integral β_{17} should – to a first approximation – leave the MO Ψ_{AS} (see Fig. 3) unaffected whereas Ψ_{SA} should be destabilized and thus be occupied by the unpaired electron. (Note that this perturbational model, at the limit $\beta_{17} = 1$, corresponds to the MO-model of heptalene).

Taking $\beta_{17} = 0.1$ and all the other $\beta_{\mu\nu} = 1$ one finds, in the *McLachlan* approximation, the calculated coupling parameters reported in Table 1. The assignment of the two large couplings is the following: the largest coupling ($a = -3.64$ G) is assigned, as in heptalene, to the protons on centers 3, 5, 9, 11; the other large coupling ($a' = 2.24$ G) is assigned to the protons on centers 2, 6, 8, 12. This will be discussed in more detail below. The two small coupling constants (each corresponding to a set of two equivalent protons) cannot be unambiguously assigned. Nevertheless, the existence of a relatively small coupling constant for protons H(4), H(10) provides evidence that, similarly to heptalene and in agreement with the calculation, the MO Ψ_{SA} is occupied by the unpaired electron.

4. π-Bond delocalization in the radical anions of 4n-annulenes. – It might be worthwhile to recall here that the analogous π-bond situation (*i.e.* π-bond delocalization) was found for the radical anions of other 4n-annulenes such as [16]annulene [7] and cycl[3.3.3]azine (also a [12]annulene-derivative [10]).

As outlined above the delocalized structure of the radical anions of heptalene and 1,7-methano-[12]annulene has been deduced from the observation that the experimental coupling constants reflect the C_{2v}-symmetry. We would, in principle, obtain the same result, if the rate of interconversion of the equivalent localized structures were fast on the ESR. time scale. This is indeed the case for the neutral hydrocarbons **1** and **2**: as detected from temperature-dependent NMR.-measurements **1** and **2** exhibit a fast and reversible π-bond shift. At −100°, the lowest temperature at which the ESR.-spectra of $\mathbf{1}^{\dot{-}}$ and $\mathbf{2}^{\dot{-}}$ have been measured, there is no indication of some exchange process [11]. Therefore we conclude, that in analogy to the situation in other 4n-annulenes, the delocalized structures of the radical anions $\mathbf{1}^{\dot{-}}$ and $\mathbf{2}^{\dot{-}}$ are energetically preferred.

Another argument in favour of π-bond delocalization can be obtained from a calculation of the spin densities. Regardless of the bridging effect, only for a delocalized structure we find an alternation of centers with high and low AO-coefficient. In an analogous calculation for a localized perimeter the AO-coefficients around the ring are of comparable magnitude. We can allow for an interconversion of the equivalent localized structures by averaging the relevant spin densities. However, the agreement between the calculated (averaged) and experimental couplings becomes much worse than it is the case for the π-bond delocalized structure.

Because of the nodal properties of the non-bonding MO's the argument given above should be generally valid for the radical anions of 4n-annulenes: if 2n-protons

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[1]) In order to reproduce the electronic consequences of the bridging in the HMO-model one can either modify the *Coulomb*-Integrals at the bridgehead positions thus simulating the inductive effect of the substituent or one can introduce a small resonance interaction between C(1) and C(7).

of the $C_{4n}H_{4n}$-ring exhibit a weak and alternatively 2n-protons a strong coupling with the unpaired electron, the radical anion can be assumed to be delocalized.

Finally, it seems worthwhile to point out the following structural difference of the bridged and non-bridged annulene-radicals: in the more or less rigid molecules discussed here one has no problem-as for example in [16]annulene-to establish the unknown configuration of the radical anion with respect to the neutral molecule. However, when using MO-models, a complication common to all annulene-type compounds arises from the fact that the symmetry of the approximate one-electron Hamiltonian is no longer governed by the ring topology of the molecule but by geometric deformations of conformational and configurational origin. The HMO-model is then advantageously modified using variable resonance integrals.

5. The effect of non-planarity in the ESR.-spectrum of the bridged [12]annulene. – The significant discrepancy between the calculated and the experimental hyperfine coupling constants for the radical anion of 1,7-methano-[12]annulene is due to the fact that the perimeter cannot adopt a fully planar geometry. Even when more sophisticated MO-methods are applied to calculate the spin densities, the application of the *McConnell*-equation is only valid for a planar perimeter. Non-planarity is accompanied by a loss of σ/π-orthogonality, what can induce a direct transfer of spin density on to the hydrogen atoms.

$$a_{H(\mu)} = Q \cdot \rho_\mu + A \cdot \rho_\mu \langle \cos^2 \phi \rangle + B \cdot \rho_\nu \langle \cos^2 \theta_{\mu\nu} \rangle + B \cdot \rho_{\nu'} \langle \cos^2 \theta_{\mu\nu'} \rangle$$

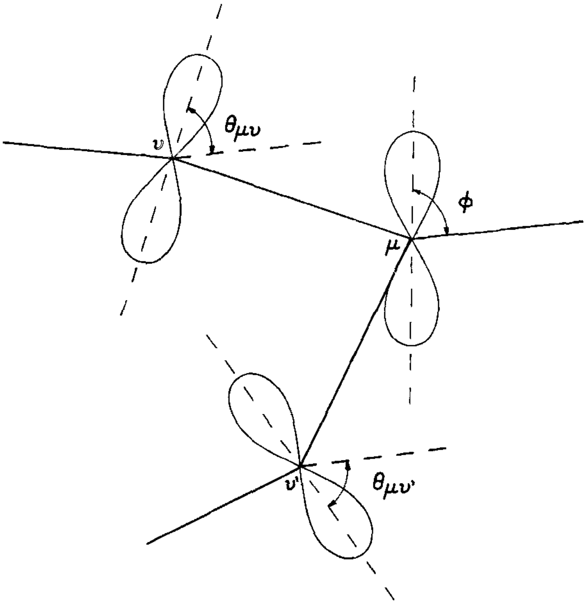

Fig. 4. *The application of the modified* McConnell-*equation for non-planar π-radicals.* ρ_μ (ρ_ν, $\rho_{\nu'}$) are the spin densities at the ring centres μ (ν, ν')

The contributions to the final spin density which are due to σ/π-polarization and due to such a 'through-space' effect can differ in sign (see below).

This interpretation could be confirmed by the analysis of several π-radicals with non-planar geometry. One example is 1,6-methano-[10]annulene, the 10π-system which is analogous to compound **2**. For the case of 1,6-methano[10]annulene it proved useful to modify the *McConnell*-equation, as it is shown in Fig. 4 [12]. A detailed interpretation of this relation has been given elsewhere [13] [14]. The A-term will always diminish the value of the coupling constant $a(H-\mu)$, while the B-terms can increase or diminish the spin density on the proton depending on the sign of the spin densities ϱ_μ and ϱ_ν at the neighbouring centers. The ring center C(2) in the radical anion $\mathbf{2}^{\dot{-}}$ is surrounded by π-centers with large positive spin densities whereas the spin density ϱ_2 itself is small. Therefore one might expect for a(H(2)) a positive sign. Consequently, we assign $a' = |2.24|$ G (with positive sign) to position 2. The assignment of $a = -3.64$ G to center 3 is now compelling. The reduction of the absolute value of the largest coupling (-3.64 G) relative to the calculated parameter or relative to the analogous coupling in heptalene can be interpreted by the A-term in the modified *McConnell*-equation.

6. Conclusions. – If, at a first glance, the ESR.-spectra of the heptalene and 1,7-methano-[12]annulene radical anions seem to be quite different, they have not to be explained by a significant redistribution of spin densities when going from one π-system to the other. The apparent differences in the two spectra result from the non-planar geometry of the bridged [12]annulene (**2**) while the agreement of experimental and calculated coupling constants in the heptalene radical anion indicates that this species, contrary to neutral heptalene, is most likely planar. It is worthwhile mentioning that INDO-calculations fully support the conclusions concerning the spin density distribution which we derived from the one-electron MO-model. An interpretation of the UV.-spectra of the radical anions of heptalene and 1,7-methano-[12]annulene also points to π-delocalization in these species [5].

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262. Interaction of Ophidian L-Amino Acid Oxidase with its Substrates and Inhibitors: Role of Molecular Geometry and Electron Distribution[1])

Communication 6 on ophidian L-amino acid oxidases[2])

by **E. Albert Zeller, Lorraine M. Clauss**[3]), and **John T. Ohlsson**[4])

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Dedicated to Professor *Franz Leuthardt*, Ph. D., M.D.h.c., University of Zurich

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Summary. Molecular activities, determined polarographically for the degradation of phenylalanine and 21 meta- and para-substituted derivatives by crystalline L-amino acid oxidase, yielded a linear *Hammett* plot of positive slope. However, the presence of large moieties in the para-position led to negative deviations which were linearly correlated with *van der Waals'* radius of the substituent. This suggested that the large substituents cause the substrate molecules to be displaced from their normal (eutopic, productive) position at the active site, resulting in lower velocities. In analogous experiments with competitive inhibitors (ring-substituted benzoic and phenylacetic acids), the logarithm of K_i was found to be a linear function of *Hansch*'s hydrophobic constant π. Lines of different slope characterized the meta- and para-derivatives, suggesting that the nature of the substituent affects the strength of hydrophobic binding, while the locus determines the orientation of the inhibitor on the active site. An analysis of the data reported here and in the literature for meta- and para-compounds supports the idea that the geometry of the ring-substituted substrate affects the orientation of the molecule on the active site, which may in turn determine which step of the reaction sequence becomes rate-limiting.

Whenever a substrate molecule is bound to the active site of an enzyme, a catalytic event is presumed to take place. During the Fifties, however, an increasing number of observations obtained with several enzymes suggested the existence of enzyme-substrate complexes which are incapable of breaking down to products and free enzyme. A series of papers on the specificity of chymotrypsin by *Niemann et al.* and reviewed by *Niemann* in 1964 [5], stand out as milestones in this development. During the same period of time, a considerable body of experimental data on oxidative deamination was collected in this laboratory. This information was interpretable

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