

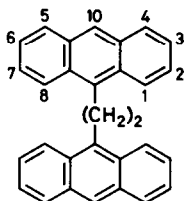
RADICAL TRIANIONS OF CONJUGATED HYDROCARBONS,
NEW MODELS FOR ESR SPECTROSCOPY

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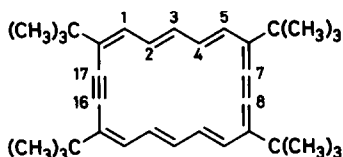
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Abstract: The preparation and spectroscopic characterization of radical trianions derived from conjugated hydrocarbons are discussed.

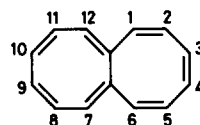
Ionic derivatives of conjugated hydrocarbons, like radical cations, dications, radical anions and dianions, have proven of great value in testing theoretical predictions by means of magnetic resonance spectroscopy (NMR [1] ESR [2]). Higher negatively charged species (radical trianions, tetraanions) have long been elusive although their inclusion in the above studies would be desirable. The preparation and NMR spectroscopic characterization of various tetra-anionic π -systems by K. Müllen and his group [3] prompted us to study the ESR spectroscopic properties of related radical trianions. The choice of the substrates 1-6 has proven advantageous for documenting the most significant aspects: the spin density distribution, the energetic sequence of the molecular orbitals and the ion pairing.



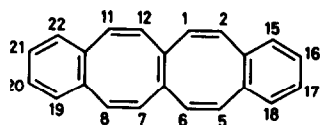
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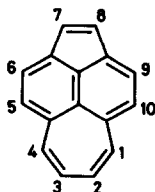
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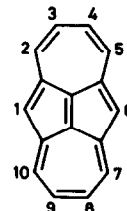
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Experimental procedures: The radical ions were prepared via reduction of the neutral compounds (1[4], 2[5], 3[6], 4[7], 5[8], 6[9]) with lithium, potassium or sodium in ethereal solvents such as THF (tetrahydrofuran), DME (1,2-dimethoxyethane) or a mixture of DME and HMPA (hexamethyl phosphoric triamide). The formation of the radical trianions was monitored by ESR spectroscopy in order to avoid overreduction to the tetraanions. The coupling constants listed in the Table and the numbers of equivalent protons have been evaluated by an analysis of the ESR spectra which is assisted for all radical trianions by ENDOR spectra. Also included in the Table are the calculated π -spin populations (ρ_{μ}) and the proportionality factors (Q_{C-H}) which result from the McLachlan procedure [10] and the McConnell relationship [11], respectively.

Availability and persistence of the radical trianions: One anticipates that in cases where the tetraanions of the compounds 1-6 are already known, the respective radical trianions can be prepared in a concentration necessary for an ESR spectroscopic characterization. This statement holds only for 1,2-dianthrylethane (1⁴⁻[15]), didehydro[18]annulene (2⁴⁻[3a]), dibenz[c,j]octalene (4⁴⁻[7]) and acepleiadylene (5⁴⁻[3b]). A remarkable exception, however, is the radical trianion of octalene 3 (3⁴⁻[3c]). Despite the persistence of 3²⁻ and 3⁴⁻ the preparation of 3⁻ and 3³⁻ by metallic reduction failed. This finding indicates a nearly quantitative disproportionation of 3⁻ to 3 and 3²⁻ and of 3³⁻ to 3²⁻ and 3⁴⁻. This behaviour of 3⁻ and 3³⁻ has already been shown in the NMR investigation of 3²⁻ and 3⁴⁻[3c]. The preparation of 3⁻ is possible by an electrolytic reduction of 3 in DMF (dimethylformamide) with $n\text{-Bu}_4\text{N}^+\text{ClO}_4^-$ as the supporting salt. The higher charged ions of 3 are unstable under these conditions with respect to fragmentation [13]. The highest charged ion from dicycloheptapentalene (6) known thus far was the dianion 6²⁻. Further reduction of 6²⁻ leads to the radical trianion 6³⁻. The coupling constants for 6³⁻ sensitively depend on the counterion and the solvent. Two examples (DME/Li; DME/Na) are given in the Table. While 6³⁻ is persistent in pure ethereal solvents, it is protonated in mixtures of DME/HMPA [13].

Influence of the counterions For steric reasons, one expects the radical trianions to interact strongly with the alkali metal counterions. In the case of 2³⁻, 4³⁻ and 5³⁻, the influence of adjacent counterions on the spin distribution appears to be negligible to a first approximation. In 1³⁻, however, the interaction with the counterion induces a localization of the spin density on one anthracene moiety. This finding follows from the coupling constants which nearly double on going from 1⁻ to 1³⁻ and which resemble those of the radical anion of ethylantracene (7⁻). In 6³⁻ one observes 6 coupling constants. Obviously the adjacent counterions polarize the spin density and/or the charge density in such a way that the system no longer reflects the D_{2h} symmetry of the parent compound 6.

Spin distribution: Due to the fact that the spin density in 1³⁻ is localized on one anthracene unit, the description of 1³⁻ as a radical anion of ethylantracene, slightly disturbed by the linkage to an anthracene dianion is straightforward. Consequently, a calculation of the coupling constants for 1³⁻ can adopt the parameters usually adequate for radical anions. The radical trianions of 2, 4, 5, 6 provide additional information about the applicability of theoretical models to highly charged species. The qualitative agreement between the calcula-

Table: Coupling constants (in mT) for the radical anions ($\underline{1}^{\cdot-}, \underline{2}^{\cdot-}, \underline{2}^{3\cdot-}, \underline{4}^{\cdot-}, \underline{5}^{\cdot-}, \underline{6}^{\cdot-}, \underline{7}^{\cdot-}$) and the radical trianions ($\underline{1}^{3\cdot-}, \underline{2}^{3\cdot-}, \underline{4}^{3\cdot-}, \underline{5}^{3\cdot-}, \underline{6}^{3\cdot-}$). Calculated spin populations for the next lowest unoccupied molecular orbitals (ρ_{μ} :NLUMO) and proportionality factors (Q_{C-H} in mT) for the radical trianions.

	$\underline{1,4,5,8}^a$	$\underline{2,3,6,7}^a$	$\underline{10}^a$	$\underline{CH_2}$	Q_{C-H}	
$\underline{1}^{\cdot-}$ (DME/HMPA:K ⁺)[15]	0.184(4) ^b	0.121(4)	0.098(4)	0.059(4)	0.264(2)	0.096(4)
$\underline{1}^{3\cdot-}$ (DME:K ⁺)[15]	0.283(4)	0.146(4)	0.472(1)	0.228(2)	0.029(2)	
$\underline{7}^{\cdot-}$ (DME:K ⁺)[16]	0.29(2)	0.27(2)	0.14(2)	0.17(2)	0.525(1)	0.25(2)
	$\underline{1,5,10,14}^a$	$\underline{2,4,11,13}^a$	$\underline{3,12}^a$	$\underline{(CH_2)_3}^c$		
$\underline{2}^{\cdot-}$ (DME:K ⁺)[17]	0.087(4)	0.402(4)	0.135(2)	0.008 ^c		
$\underline{2}^{3\cdot-}$ (THF:K ⁺)	0.323(4)	0.089(4)	0.332(2)	0.011 ^c		2.41
ρ_{μ} :NLUMO ^d	0.124	-0.031	0.169			
	$\underline{1,6,7,12}^a$	$\underline{2,5,8,11}^a$	$\underline{3,4,9,10}^a$	$\underline{15,18,19,22}^a$	$\underline{16,17,20,21}^a$	
$\underline{2}^{\cdot-}$ (DMF:n-Bu ₄ N ⁺)	0.012(4)	0.198(4)	0.081(4)			
$\underline{4}^{\cdot-}$ (DME/HMPA:K ⁺)	0.01 ^c	0.261(4)		0.098(4)	0.069(4)	
$\underline{4}^{3\cdot-}$ (DME/HMPA:K ⁺)	0.357(4)	0.027 ^c		0.046 ^c	0.161(4)	2.83
ρ_{μ} :NLUMO ^d	0.164	0.010		-0.013	0.037	
	$\underline{1,4}^a$	$\underline{2,3}^a$	$\underline{5,10}^a$	$\underline{6,9}^a$	$\underline{7,8}^a$	$\underline{a_M}^+$
$\underline{5}^{\cdot-}$ (DME:Na ⁺)[18]	0.021(2)	0.276(2)	0.08(2)	0.404(2)	0.244(2)	
$\underline{5}^{3\cdot-}$ (THF:K ⁺)	0.625(2)	0.216(2)	0.068(2)	0.068(2)	0.007 ^c	0.045(2)
ρ_{μ} :NLUMO ^d	0.306	0.080	0.040	-0.024	0.000	2.26
	$\underline{1,6}^a$	$\underline{2,5,7,10}^a$	$\underline{3,4,8,9}^a$	$\underline{a_M}^+$		
$\underline{6}^{\cdot-}$ (DME/HMPA:Li ⁺)	0.020(2)	0.064(4)	0.267(4)			
$\underline{6}^{3\cdot-}$ (DME:Li ⁺)	0.207(1)	0.173(1)	0.361(2)	0.249(2)	0.085(2)	0.043(2)
	0.190 ^e	0.305 ^e	0.064 ^e			1.71
$\underline{6}^{3\cdot-}$ (DME:Na ⁺)	0.108(1)	0.044(1)	0.209(2)	0.025(2)	0.340(2)	0.232(2)
	0.076 ^e	0.117 ^e	0.286 ^e			0.027(2)
ρ_{μ} :NLUMO ^d	0.126	0.164	0.040			

a) Positions.

b) The numbers of equivalent protons are indicated in brackets.

c) These coupling constants are unresolved in the ESR spectra. They are taken from the respective ENDOR spectra.

d) The spin populations :NLUMO for $\underline{2}^{3\cdot-}$, $\underline{5}^{3\cdot-}$ and $\underline{6}^{3\cdot-}$ are calculated with the following parameters: $\alpha_{\mu} = \alpha$, $\beta_{\mu\nu} = \beta$, $\lambda = 1.2$. For $\underline{2}^{3\cdot-}$ the bonding integrals $\beta_{7,8}$ and $\beta_{16,17}$ (triple bonds) are changed to 1.5β [17].

e) Average value of the above two coupling constants.

ted spin populations (ρ_{μ}) for the NLUMO (next lowest unoccupied molecular orbital) and the observed coupling constants in $\underline{2}^{3-}$, $\underline{4}^{3-}$ and $\underline{5}^{3-}$ is obvious (Table). The HMO model therefore provides the correct sequence of LUMO (lowest unoccupied molecular orbital) and NLUMO. The mechanism of π - π -spin polarization in radical trianions is handled adequately by the McLachlan procedure. A quantitative correlation of spin populations and coupling constants by the McConnell relationship holds for the planar trianions $\underline{2}^{3-}$ and $\underline{5}^{3-}$ ($Q_{C-H} \approx 2.3$ mT). As in radical anions [14], deviations from planarity account for the discrepancies in $\underline{4}^{3-}$. In $\underline{6}^{3-}$, where ion pair formation lowers the original symmetry (see above), one has to refer to the average value of two coupling constants belonging to two equivalent protons in the neutral compound (Table). Analogous arguments are commonly applied to the interpretation of coupling constants in radical anions of cyclophanes [12]. The average values of the coupling constants in the lithium salt correlate satisfactorily with the calculated spin populations for the NLUMO in $\underline{6}$, whereas those of the respective sodium salt do not. These data resemble those of $\underline{6}^{\cdot-}$ and therefore reflect a spin distribution which favors a single occupancy of a LUMO-type orbital. This electronic configuration can only be realized by a change in the orbital sequence when passing from the lithium to the sodium salt. A full account of the above results will be given elsewhere [13].

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