112. Radical Ions in the Pentalene Series

Part III[1])

Three Paramagnetic Redox Stages of a Dicyclopenta[*a*,*e*]pentalene

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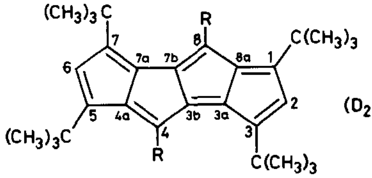
(13.IV.88)

Five redox stages have been observed for the recently synthesized 1,3,5,7-tetra(*tert*-butyl) derivative **1** of the dicyclopenta[*a*,*e*]pentalene, a novel non-alternant hydrocarbon: the radical cation $\mathbf{1}^{+\cdot}$, the neutral compound **1**, the radical anion $\mathbf{1}^{-\cdot}$, the dianion $\mathbf{1}^{2-}$, and the radical trianion $\mathbf{1}^{3-\cdot}$. Information about the electronic structure of the three paramagnetic stages, $\mathbf{1}^{+\cdot}$, $\mathbf{1}^{-\cdot}$, and $\mathbf{1}^{3-\cdot}$ is provided by the use of ESR, ENDOR, and TRIPLE resonance spectroscopy. The unpaired electron in the trianion resides mainly on the 'inner' butadiene-π-system, whereas in the cation and the anion, it is largely localized on the two 'outer' five-membered rings.

Introduction. – 1,3,5,7-Tetra(*tert*-butyl)cyclopenta[*a*,*e*]pentalene (**1**), which contains a non-alternant π-system with a $(4n + 2)$-membered perimeter, has recently been synthesized [2].



1 R = H

(D_2)**1** R = D

As shown below, **1** exists in five redox-stages, which is rather a surprising result for a relatively small π-system comprising only 14 C centers. The two diamagnetic stages, the neutral compound **1** and the dianion $\mathbf{1}^{2-}$, have been characterized previously [2]. The present paper deals with the three paramagnetic stages, the radical cation $\mathbf{1}^{+\cdot}$, the radical anion $\mathbf{1}^{-\cdot}$, and the radical trianion $\mathbf{1}^{3-\cdot}$, which have all been studied by ESR, ENDOR, and TRIPLE resonance spectroscopy. To assign the coupling constants to protons in individual positions, the corresponding 4,8-dideuterated species, $(D_2)\mathbf{1}^{+\cdot}$, $(D_2)\mathbf{1}^{-\cdot}$, and $(D_2)\mathbf{1}^{3-\cdot}$, are also included in this investigation.

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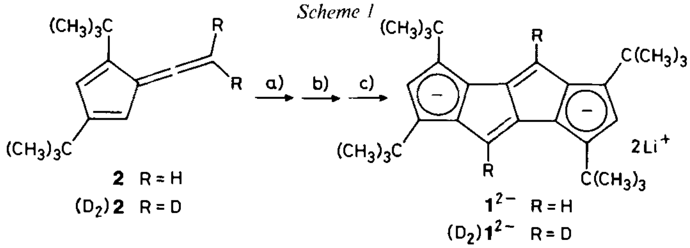
[1]) Part II: [1].

Experimental. – *Compound* (D_2)**1** was obtained by oxidation of its dianion $(D_2)\mathbf{1}^{2-}$ with $FeCl_3$ at 25°. The preparation of $(D_2)\mathbf{1}^{2-}$ was achieved analogously as $\mathbf{1}^{2-}$ from 1,3-di(*tert*-butyl)-5-vinylidene-1,3-cyclopentadiene (**2**) [2]. At first, **2** was converted into (D_2)**2** by a base-catalyzed deuteriation (a) 2 BuLi/THF–100°; b) D_2O/25°) *(Scheme 1)*.

Scheme 1



a) 10°/14 d. b) DDQ (= 2,3-dichloro-5,6-dicyano-1,4-benzoquinone)/25°/Et_2O. c) 2 Li-2,2,6,6-tetramethylpiperidide/THF/25°.

Electrochemistry. The cyclic voltammogram of **1** was taken at r.t. with MeCN as the solvent and Bu_4NBF_4 as the supporting salt. Pt disc and glassy C served for the working and counter electrode, respectively. The instrument was a *Metrohm Polarecord E56* with a *VA* Scanner *612/VA Stand 663* (scan 300 mV/s).

Preparation of Radical Ions for Spectroscopic Studies. The radical cations $\mathbf{1}^{\cdot+}$ and $(D_2)\mathbf{1}^{\cdot+}$ were generated by oxidation of the corresponding neutral compounds in CH_2Cl_2, using a variety of reagents such as $AlCl_3$, CF_3COOH, and tris(*p*-bromophenyl)ammoniumyl-$SbCl_6$. The radical anions $\mathbf{1}^{\cdot-}$ and $(D_2)\mathbf{1}^{\cdot-}$ were produced by reduction of their neutral counterparts with K in 1,2-dimethoxyethane, THF, or 2-methyltetrahydrofuran (MTHF) as well as in mixtures of these solvents with hexamethylphosphoric triamide (HMPT). A prolonged contact of the solns. with the metallic mirror in carefully purified THF or MTHF led *via* $\mathbf{1}^{2-}$ and $(D_2)\mathbf{1}^{2-}$ to $\mathbf{1}^{3\cdot-}$ and $(D_2)\mathbf{1}^{3\cdot-}$, respectively. ESR spectra were taken on a *Varian-E9* instrument, while a *Bruker-ESP-300* spectrometer was used for ENDOR and TRIPLE resonance studies.

Results and Discussion. – The cyclic voltammogram of **1** exhibits three waves in the voltage region of +1 to –2.5 V; they indicate one-electron transfers between four redox stages.

$$\mathbf{1}^{\cdot+} \underset{-e^-}{\overset{+e^-}{\rightleftarrows}} \mathbf{1} \underset{-e^-}{\overset{+e^-}{\rightleftarrows}} \mathbf{1}^{\cdot-} \xrightarrow{+e^-} \mathbf{1}^{2-}$$

$$\underset{\text{(reversible)}}{E_{1/2} = +0.55\ \text{V}} \qquad \underset{\text{(reversible)}}{E_{1/2} = -1.00\ \text{V}} \qquad \underset{\text{(irreversible)}}{E_p = -1.65\ \text{V } vs.\ \text{SCE}}$$

Under the strictly aprotic conditions employed in the preparation of the dianions and radical trianions for spectroscopic studies (see *Experimental*), a fifth redox stage is accessible through an exhaustive reduction[2].

$$\mathbf{1}^{2-} \xrightarrow{+e^-} \mathbf{1}^{3\cdot-}$$

The ESR studies of the highly persistent radical ions $\mathbf{1}^{\cdot+}$, $(D_2)\mathbf{1}^{\cdot+}$, $\mathbf{1}^{\cdot-}$, and $(D_2)\mathbf{1}^{\cdot-}$ were performed in the temperature range of 193–298 K, whereas 263 K was the upper limit for the investigation of the less stable radical trianions $\mathbf{1}^{3\cdot-}$ and $(D_2)\mathbf{1}^{3\cdot-}$. Analysis of the ESR spectra *(Figs. 1* and *2)*, which was accomplished by the ENDOR technique [3], yielded the

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[2] Proton impurities readily react with the dianions and, thus, prevent the formation of the trianions. Minute amounts of such impurities are presumably present in MeCN used as the solvent in cyclic voltammetry (causing the redox step $\mathbf{1}^{\cdot-} \rightarrow \mathbf{1}^{2-}$ to be irreversible), but they can be almost completely eliminated in dried THF or MTHF.

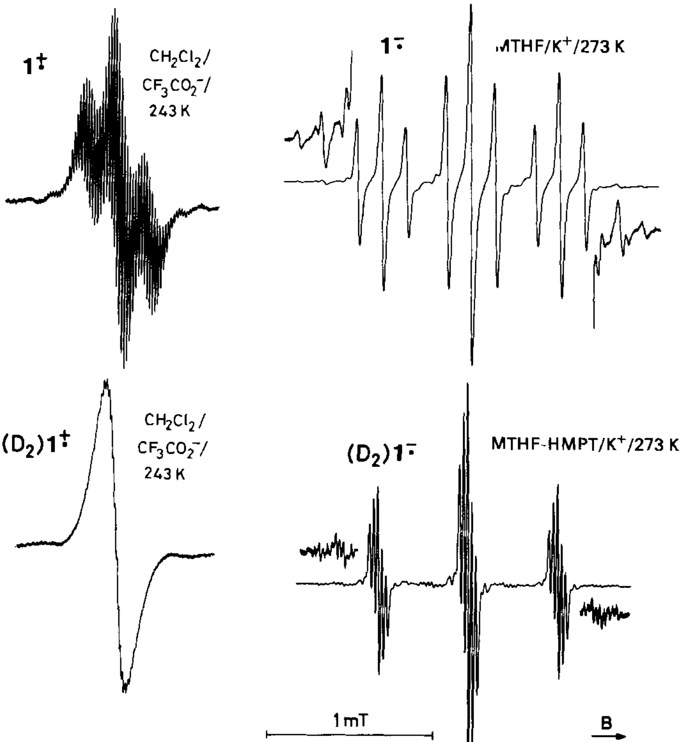


Fig. 1. *ESR spectra of the radical cations and radical anions of 1,3,5,7-tetra(*tert*-butyl)cyclopenta[*a,e*]pentalene* (**1**) *and its 4,8-dideuterio derivative (*D_2*)* **1**. Specified in each spectrum: solvent/counterion/temp. g Factor: 2.0025 ± 0.0001 for both cations and anions.

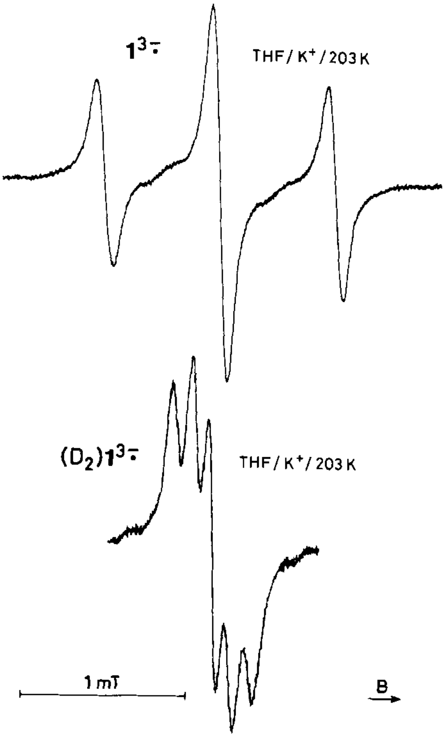


Fig. 2. *ESR spectra of the radical trianions of 1,3,5,7-tetra(*tert*-butyl)cyclopenta[*a,e*]pentalene* (**1**) *and its 4,8-dideuterio derivative (*D_2*)* **1**. Specified in each spectrum: solvent/counterion/temp. g Factor: 2.0028 ± 0.0001.

Table. *Coupling Constants* [mT] *of Protons, Deuterons, and* ^{13}*C Isotopes in the Radical Cations, Radical Anions, and Radical Trianions of 1,3,5,7-Tetra(*tert*-butyl)dicyclopenta[*a,e*]pentalene* (**1**) *and its 4,8-Dideuterio Derivative (D$_2$)* **1**a))

Position	1,5	2,6	3,7	4,8
$\mathbf{1}^{+\cdot}$	+0.017 (18 H)b))	+0.045 (2 H)	+0.017 (18 H)b))	−0.169 (2 H)
$(D_2)\mathbf{1}^{+\cdot}$				−0.026 (2 D)
$\mathbf{1}^{-\cdot}$	+0.005 (18 H)b))	−0.545 (2 H)	+0.005 (18 H)b))	−0.151 (2 H)
	−0.43 (2 ^{13}C)	+0.72 (2 ^{13}C)	−0.051 (2 ^{13}C)	
$(D_2)\mathbf{1}^{-\cdot}$				−0.024 (2 D)
$\mathbf{1}^{3-\cdot}$	+0.007 (18 H)b))	+0.021 (2 H)	+0.007 (18 H)b))	−0.730 (2 H)
$(D_2)\mathbf{1}^{3-\cdot}$				−0.112 (2 D)

a) Conditions (solvent/counterion/temp.) as for the ESR spectra in *Figs. 1* and *2*. Exper. error: ±0.001 mT for the coupling constants < 0.1 mT and 1% for those > than 0.1 mT.

b) Protons of *t*-Bu groups.

proton and deuteron coupling constants listed in the *Table*. Their signs were provided by general TRIPLE resonance (for a review, see [3]) on the assumption that the absolutely largest value is negative in each case. For $\mathbf{1}^{-\cdot}$ and $(D_2)\mathbf{1}^{-\cdot}$, three ^{13}C coupling constants could also be determined from the satellites in the ESR spectra *(Fig. 1)*. The signs and the assignments of these values to ^{13}C isotopes in the individual sites *(Table)* rely on the well-known relationships [4a] between the ^{13}C coupling constants and the π-spin populations at the C-atoms. These populations have been derived from the experimental proton data [4b] and the theoretical models presented below.

The coupling constants of the protons and deuterons in $\mathbf{1}^{-\cdot}$, $(D_2)\mathbf{1}^{-\cdot}$, $\mathbf{1}^{3-\cdot}$, and $(D_2)\mathbf{1}^{3-\cdot}$ were markedly dependent on the temperature and the solvent. Such a dependence has, in general, been observed for the radical anions of non-alternant hydrocarbons [5]. It is presumably due to their association with the counterions K^+, since ion pairings of this kind influence the coupling constants and are in turn sensitive to changes in the environment [6]. For $\mathbf{1}^{-\cdot}$ in THF, the ion pairing became apparent when Cs^+ replaced K^+ as the counterion; a ^{133}Cs coupling constant was then evident which, at 243 K, had the value of 0.15 mT.

Interestingly, line broadenings were observed in the ESR spectra of $\mathbf{1}^{-\cdot}$ and $(D_2)\mathbf{1}^{-\cdot}$ at low temperatures, whereby the affected hyperfine components differed from one solvent to another. Computer simulations [7] suggest that more than just one dynamic process is responsible for these broadenings. Three of such processes can be considered: *i)* migration of K^+ between preferred positions in the proximity of the radical anion [6] [8], *ii)* hyperfine anisotropy which is not completely averaged out in viscous solutions of radicals with bulky substituents [9], and *iii)* fast exchange between structures with localized double bonds and lower symmetry. For the neutral dicyclopenta[*a,e*]pentalene, such structures should be energetically favored relative to the delocalized form. To our knowledge, a dynamic process with an underlying double-bond fixation has not yet been revealed for a radical ion on the hyperfine time-scale (in this context, see [10]).

The experimental data in the *Table* indicate that the highest π-spin populations are located on the following C-atoms: C(1), C(3), C(5), and C(7) in $\mathbf{1}^{+\cdot}$, C(2) and C(6) in $\mathbf{1}^{-\cdot}$, and C(4) and C(8) in $\mathbf{1}^{3-\cdot}$.

These spin distributions reflect the shapes of the HOMO, LUMO, and NLUMO (next lowest unoccupied MO) of dicyclopenta[*a,e*]pentalene. They are illustrated by a

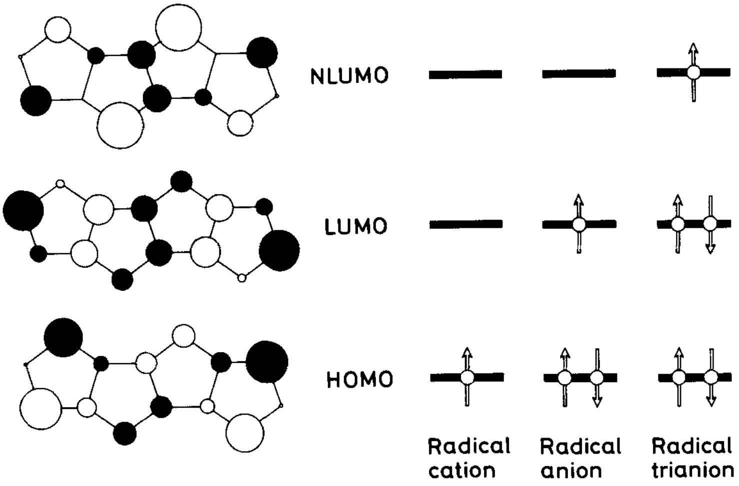


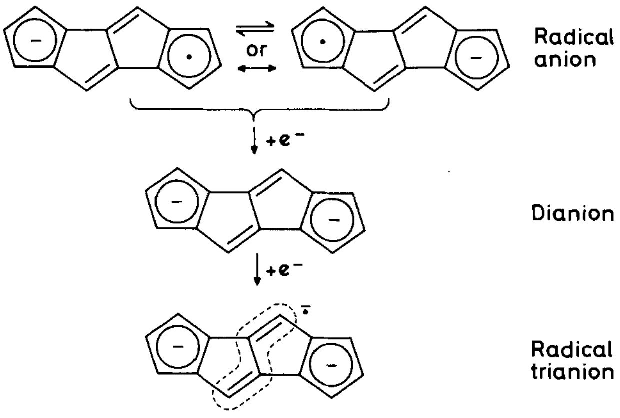
Fig. 3. *Schematic presentation of the HOMO, LUMO, and NLUMO of dicyclopenta[*a,e*]pentalene and the occupancy of these orbitals in the radical cation, radical anion, and radical trianion*

schematic presentation of the three orbitals *(Fig. 3)* which, to a large extent, has been based on a *Pariser-Parr-Pople (PPP)* calculation [11]. Similar diagrams were obtained using the *Hückel* model in which, however, the HOMO and LUMO have almost the same energy. Such a near-degeneracy does not occur when the *PPP*-method is applied.

If dicyclopenta[*a,e*]pentalene is divided into the two 'outer' five-membered rings and an 'inner' butadiene π-system, the structures of the mono-, di-, and trianions can be described by the formulas drawn underneath *(Scheme 2)*.

According to these formulas, the unpaired electron in the radical anion should favor the 'outer' five-membered rings. In the dianion, each of the two rings ought to bear one negative charge, a statement which is compatible both with MO calculations [12a] (for the MO method, see [12b]) and the ^{13}C-NMR spectra of $\mathbf{1}^{2-}$ and $(D_2)\mathbf{1}^{2-}$. Whereas, on going from **1** and $(D_2)\mathbf{1}$ to $\mathbf{1}^{2-}$ and $(D_2)\mathbf{1}^{2-}$, the chemical shifts of the ^{13}C isotopes in the 'inner'

Scheme 2



butadiene π-system (C(3b), C(4), C(7b), and C(8)) remain almost unchanged ($\Delta\delta = 0$–3 ppm), a high-field shift $\Delta\delta$ of *ca.* 40 ppm is observed at the tertiary C-atoms in the two 'outer' five-membered rings (C(2) and C(6)) and that of 17–24 ppm at the quarternary C-atoms in these rings (C(1), C(3), C(3a), C(4a), C(5), C(7), C(7a), and C(8a)). With both 'outer' five-membered rings being negatively charged, the additional unpaired electron in the radical trianion should be accommodated by the 'inner' butadiene π-system, and, expectedly, the coupling constant of the 4,8-protons in $\mathbf{1}^{3\dot{-}}$ (−0.730 mT) closely resembles the corresponding value for the radical anion of (*E*)-buta-1,3-diene (−0.762 mT) [13]3). The hyperfine data for $\mathbf{1}^{\dot{-}}$ and $\mathbf{1}^{3\dot{-}}$, thus, provide a further example confirming the rule that the bulk of spin population in the radical anion and the radical trianion is located in different parts of the molecule [14].

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* and the *Deutsche Forschungsgemeinschaft.*

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3) The negative sign of this value is required by theory.