63. Effects of Non-planarity in the Radical Anions of Tribenzo[*a,c,e*]cyclooctenes

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Dedicated to Prof. *Edgar Heilbronner* on the occasion of his 70th birthday

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Reduction of tribenzo[*a,c,e*]cyclooctene (**2**) and its 2,3- and 1,4-dimethyl derivatives (**4** and **5**), as well as of 1,1-dimethyl-10,11-propane-2,2-diylidene-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene (**6**) and its 5,6-didehydro derivative (**7**) was followed by cyclic voltammetry. The radical anions of these compounds and those of their derivatives (D)**2**, (D)**5**, and (D)**6**, deuterated at C(9) in **2** and **5** or in the corresponding position of **6**, have been characterized with the use of ESR, ENDOR, and TRIPLE-resonance spectroscopy. The cyclic-voltammetric and proton-hyperfine data are consistent with the increasing deviations of the radical anions from planarity in the order $\mathbf{6}^{\overline{\cdot}}$, $\mathbf{7}^{\overline{\cdot}} < \mathbf{2}^{\overline{\cdot}}$, $\mathbf{4}^{\overline{\cdot}} < \mathbf{5}^{\overline{\cdot}}$. These deviations, due to steric H$\leftrightarrow$H ($\mathbf{2}^{\overline{\cdot}}$, $\mathbf{4}^{\overline{\cdot}}$) or H$\leftrightarrow$Me ($\mathbf{5}^{\overline{\cdot}}$) interferences in the *peri*-positions 1$\leftrightarrow$14 and 4$\leftrightarrow$5, are removed in $\mathbf{6}^{\overline{\cdot}}$ and $\mathbf{7}^{\overline{\cdot}}$ by the introduction of bridging groups. The non-planarity affects the thermodynamic and kinetic stabilities of the radical anions and causes a shift in the π-spin distribution away from that benzene ring which is linked to the two others by the essential single bonds C(4a)–C(4b) and C(14a)–C(14b). This finding suggests that the steric hindrance in $\mathbf{2}^{\overline{\cdot}}$, $\mathbf{4}^{\overline{\cdot}}$, and $\mathbf{5}^{\overline{\cdot}}$ is alleviated by twisting this ring out of coplanarity with the remaining (*Z*)-stilbene-like π-system.

Introduction. – The eight-membered ring in benzo derivatives of cyclooctatetraene has a tub-like shape resembling the C-framework of the parent compound. This statement holds for dibenzo[*a,e*]cyclooctene (**1**) [1], tribenzo[*a,c,e*]cyclooctene (**2**) [2], and tetraphenylene (**3**) [1] [3]. The tendency of cyclooctatetraene to flatten upon the uptake of additional electrons [4] [5] is shared by its benzo derivatives. Electrochemical [6] and ESR studies [7] strongly suggest that the radical anion $\mathbf{1}^{\overline{\cdot}}$ is planar. By contrast, severe steric strain prevents the eight-membered ring in $\mathbf{3}^{\overline{\cdot}}$ from adopting a planar geometry, so that the spin distribution in this radical anion is best described in terms of four weakly coupled benzene rings [8] [5]. With respect to planarity, the radical anion, $\mathbf{2}^{\overline{\cdot}}$, of the tribenzocyclooctene falls between its dibenzo- and tetrabenzo-counterparts $\mathbf{1}^{\overline{\cdot}}$ and $\mathbf{3}^{\overline{\cdot}}$, as flattening of the eight-membered ring in $\mathbf{2}^{\overline{\cdot}}$ should be more difficult than in $\mathbf{1}^{\overline{\cdot}}$, but considerably easier than in $\mathbf{3}^{\overline{\cdot}}$. It is obvious that the steric strain in $\mathbf{2}^{\overline{\cdot}}$ arises primarily from the spatial interference of the H-atoms in the *peri*-positions 1$\leftrightarrow$14 and 4$\leftrightarrow$5. Suitable reference species for the studies of the effect of non-planarity are, therefore, the radical anions of the recently synthesized 1,4-dimethyltri-

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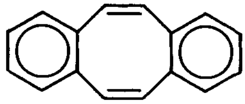

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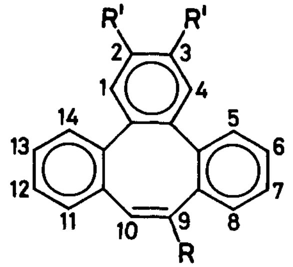
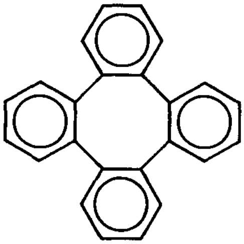


2 R=R'=H
(D)2 R=D, R'=H
4 R=H, R'=Me



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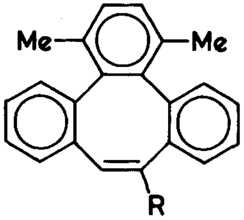
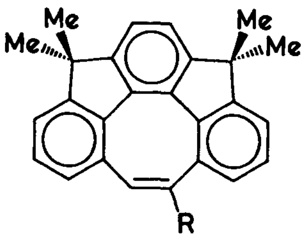
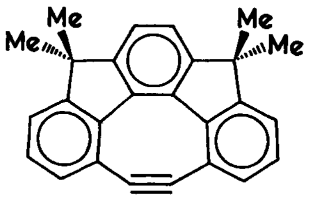


5 R=H
(D)5 R=D



6 R=H
(D)6 R=D



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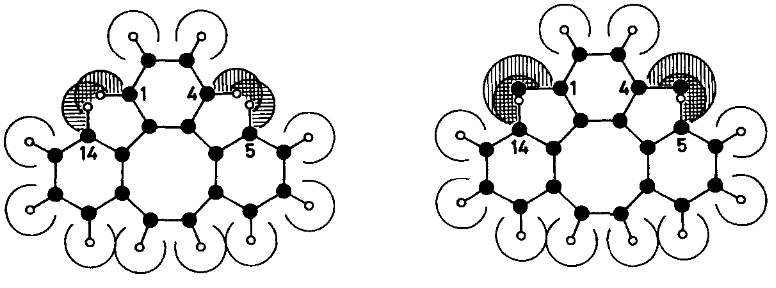
benzo[*a,c,e*]cyclooctene (**5**) [9] [10] and 1,1-dimethyl-10,11-propane-2,2-diylidene-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene (**6**) [10]. Whereas in **5** the steric hindrance in the *peri*-positions is enhanced by the 1,4-dimethyl substitution (*Fig.1*), it is removed in **6** through the replacement of the four interfering *peri*-H-atoms by the two bridging propane-2,2-diylidene groups, so that the tribenzocyclooctene π-system of this molecule is planar [11]. Therefore, the radical anion $\mathbf{6}^{\overline{\cdot}}$ is also expected to be planar, while deviations from planarity should be more pronounced in $\mathbf{5}^{\overline{\cdot}}$ than in $\mathbf{2}^{\overline{\cdot}}$.



2 **5**

Fig. 1. *Steric hindrance to planarity in* **2** *and* **5**. The H-atoms in the Me substituents of **5** are omitted for clarity.

Here, we describe ESR, ENDOR, and TRIPLE-resonance studies of **2**$^{\overline{\cdot}}$, **5**$^{\overline{\cdot}}$, and **6**$^{\overline{\cdot}}$. In order to verify assignments of the coupling constants to protons in individual positions of these ions, analogous studies have been performed on the radical anions of the derivatives (D)**2**, (D)**5**, and (D)**6**, deuterated at C(9) in **2** and **5** and in the corresponding position of **6**, as well as on those of 2,3-dimethyltribenzo[*a,c,e*]cyclooctene (**4**) and 1,1-dimethyl-10,11-propane-2,2-diylidene-5,6-didehydro-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]-fluorene (**7**) [12].

Results and Discussion. – *Reduction Potentials.* Cyclic voltammograms of tribenzo[*a,c,e*]cyclooctene (**2**) and its dimethyl derivatives **4** and **5** exhibited irreversible waves upon reduction on a dropping mercury electrode in MeCN at ambient temperature (supporting salt: Et_4NClO_4; counter-electrode: glassy carbon). On the other hand, reversible waves were observed in the cyclic voltammograms of 1,1-dimethyl-10,11-propane-2,2-diylidene-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene (**6**) and its didehydro derivative **7** under the same conditions. *Table 1* gives the potentials, E_p, of the reduction peaks of **2**, **4**, and **5**, as well as the half-wave potentials, $E_{1/2}$, of **6** and **7** which are by 0.6 to 0.7 V less negative. Thus, **6**$^{\overline{\cdot}}$ and **7**$^{\overline{\cdot}}$ are easier to form and longer-lived than **2**$^{\overline{\cdot}}$, **4**$^{\overline{\cdot}}$, and **5**$^{\overline{\cdot}}$, *i.e.*, they are both thermodynamically and kinetically more stable. This finding is readily rationalized in terms of distinct differences in the geometry of these radical anions. Whereas the planarity of **6**$^{\overline{\cdot}}$ and **7**$^{\overline{\cdot}}$ is already achieved in the corresponding neutral compounds, a substantial flattening of **2**$^{\overline{\cdot}}$, **4**$^{\overline{\cdot}}$, and **5**$^{\overline{\cdot}}$ is sterically hindered upon their formation from their tub-shaped precursors.

Table 1. *First Reduction Potentials,* E_p *or* $E_{1/2}$ ([V] *vs.* SCE)[a]), *of* **2** *and* **4**–**7**

E_p (irreversible)				$E_{1/2}$ (reversible)	
2	**4**	**5**		**6**	**7**
–2.390	–2.455	–2.580		–1.745	–1.785

a) Exper. error: ±0.005.

It is noteworthy that the shift to negative E_p values on going from **2** to **5** is as large as 0.19 V, while that on passing from **2** to **4** is only 0.065 V. Assuming that such a shift is caused by the destabilizing inductive effect of a methyl substituent on the energy of the lowest unoccupied orbital (LUMO) ψ_j of **2**, it should, according to the first-order perturbation treatment, be proportional to the squared LCAO-coefficient $c_{j\mu}^2$ at the substituted centre μ for this orbital [13]. With the use of MO models presented below, one can readily show that the shift observed upon 2,3-dimethyl substitution in **2**, to yield **4**, thus corresponds to the expected inductive destabilization of the LUMO. On the other hand, a substantially smaller shift is predicted for 1,4-dimethyl substitution in **2** to give **5**, as the $c_{j\mu}^2$ values at $\mu = 1$ and 4 are four times smaller than those at $\mu = 2$ and 3 (see below). Evidently, this prediction is in a sharp disagreement with experiment. Without doubt, the considerably more negative reduction potential, E_p, of **5**, as compared to those of **2** and **4**, is due to an increased hindrance to achieve planarity by the dimethyl substitution in the congested positions 1 and 4 (*Fig. 1*).

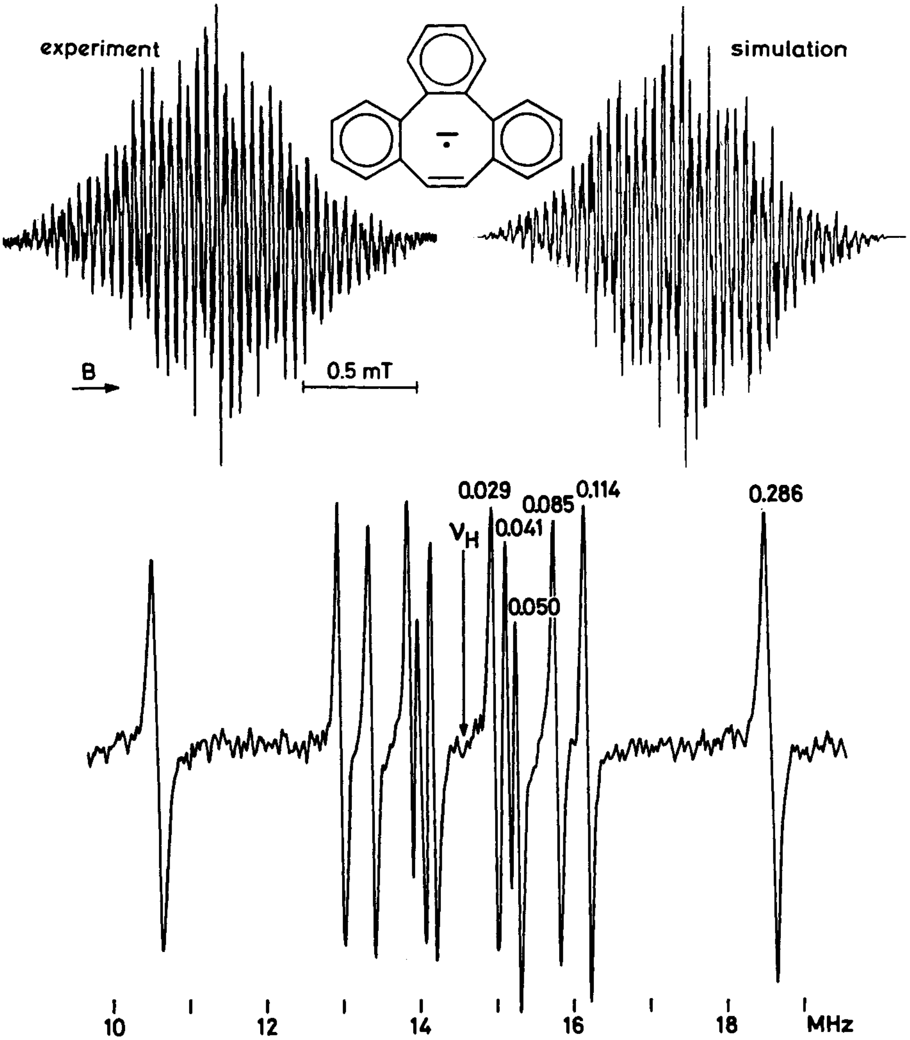


Fig. 2. *ESR* (top) *and* ^{1}*H-ENDOR* (bottom) *spectra of* $\mathbf{2}^{\cdot -}$. Solvent: DME; temp.: 203 K; counterion: K^+. Coupling constants [mT] used in the simulation of the ESR spectrum are indicated above the ENDOR signals and on the formula of $\mathbf{2}^{\cdot -}$ in *Fig. 4;* line-shape: *Lorentz*ian; line-width: 0.012 mT.

Proton-Coupling Constants. For ESR and ENDOR studies, the radical anions $\mathbf{2}^{\cdot -}$, (D)$\mathbf{2}^{\cdot -}$, $\mathbf{4}^{\cdot -}$, $\mathbf{5}^{\cdot -}$, (D)$\mathbf{5}^{\cdot -}$, $\mathbf{6}^{\cdot -}$, (D)$\mathbf{6}^{\cdot -}$, and $\mathbf{7}^{\cdot -}$ were generated from the corresponding neutral compounds by reaction with K metal in 1,2-dimethoxyethane (DME). The spectra taken at 203 K are exemplified by those of $\mathbf{2}^{\cdot -}$ (*Fig. 2*) and $\mathbf{6}^{\cdot -}$ (*Fig. 3*). The proton-coupling constants, $a_{H\mu}$, for $\mathbf{1}^{\cdot -}$ [7] and the radical anions, $\mathbf{2}^{\cdot -}$ and $\mathbf{4}^{\cdot -}$ - $\mathbf{7}^{\cdot -}$, dealt with in the present work are given in *Fig. 4*. The signs of these coupling constants have been determined by general TRIPLE-resonance [14], on the reasonable assumption that the largest $a_{H\mu}$ values are negative.

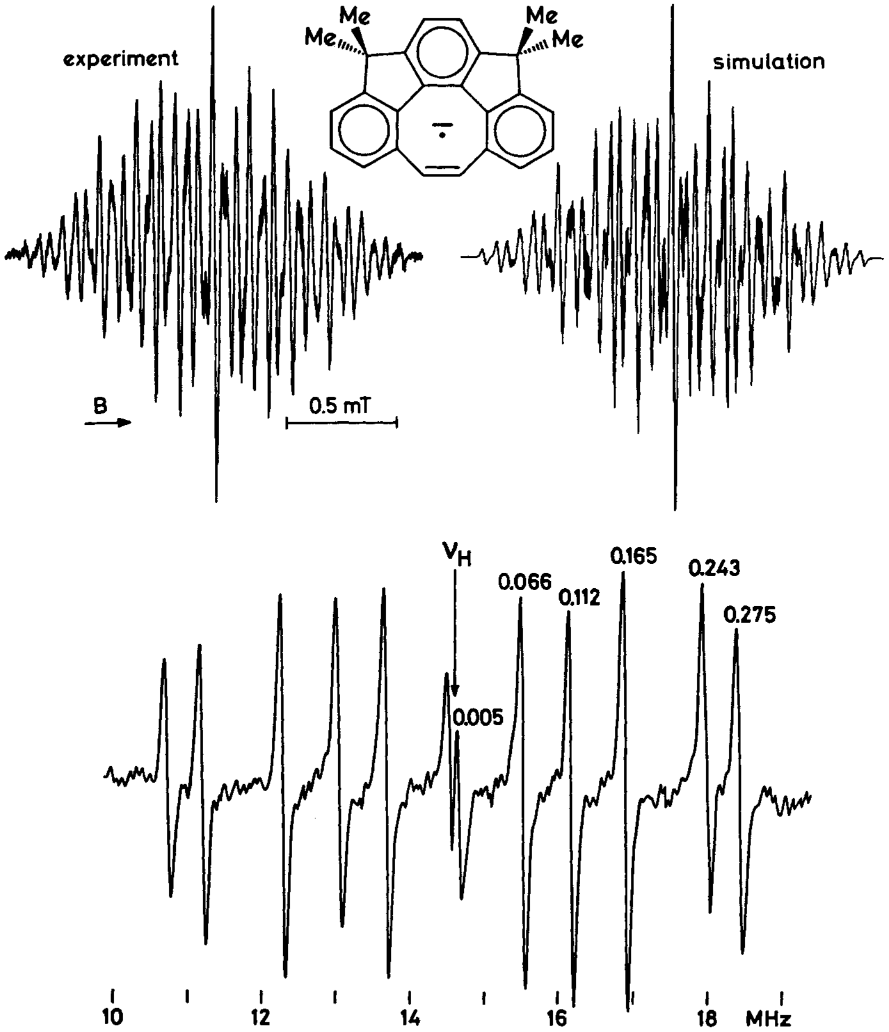


Fig. 3. *ESR* (top) *and* ^{1}*H-ENDOR* (bottom) *spectra of* **6**$^{\overline{\cdot}}$. Solvent: DME; temp.: 203 K; counterion: K$^+$. Coupling constants [mT] used in the simulation of the ESR spectrum are indicated above the ENDOR signals and on the formula of **6**$^{\overline{\cdot}}$ in *Fig. 4*; line-shape: *Lorentz*ian; line-width: 0.008 mT.

As expected, the changes in the coupling constants are substantial when structural modifications affect the congested positions 1,4 and/or 5,14, *i.e.*, on going from **2**$^{\overline{\cdot}}$ to **5**$^{\overline{\cdot}}$ or **6**$^{\overline{\cdot}}$, whereas they are much smaller when such modifications occur in other positions, *i.e.*, on passing from **2**$^{\overline{\cdot}}$ to **4**$^{\overline{\cdot}}$ or from **6**$^{\overline{\cdot}}$ to **7**$^{\overline{\cdot}}$. Assignments to protons in positions μ are straightforward if the $a_{H\mu}$ values are correlated in such a way that they continuously vary with increasing deviations from planarity in the order **6**$^{\overline{\cdot}}$ < **2**$^{\overline{\cdot}}$ < **5**$^{\overline{\cdot}}$ (*Fig. 5*). These assignments are supported by the following experimental evidence and theoretical MO models.

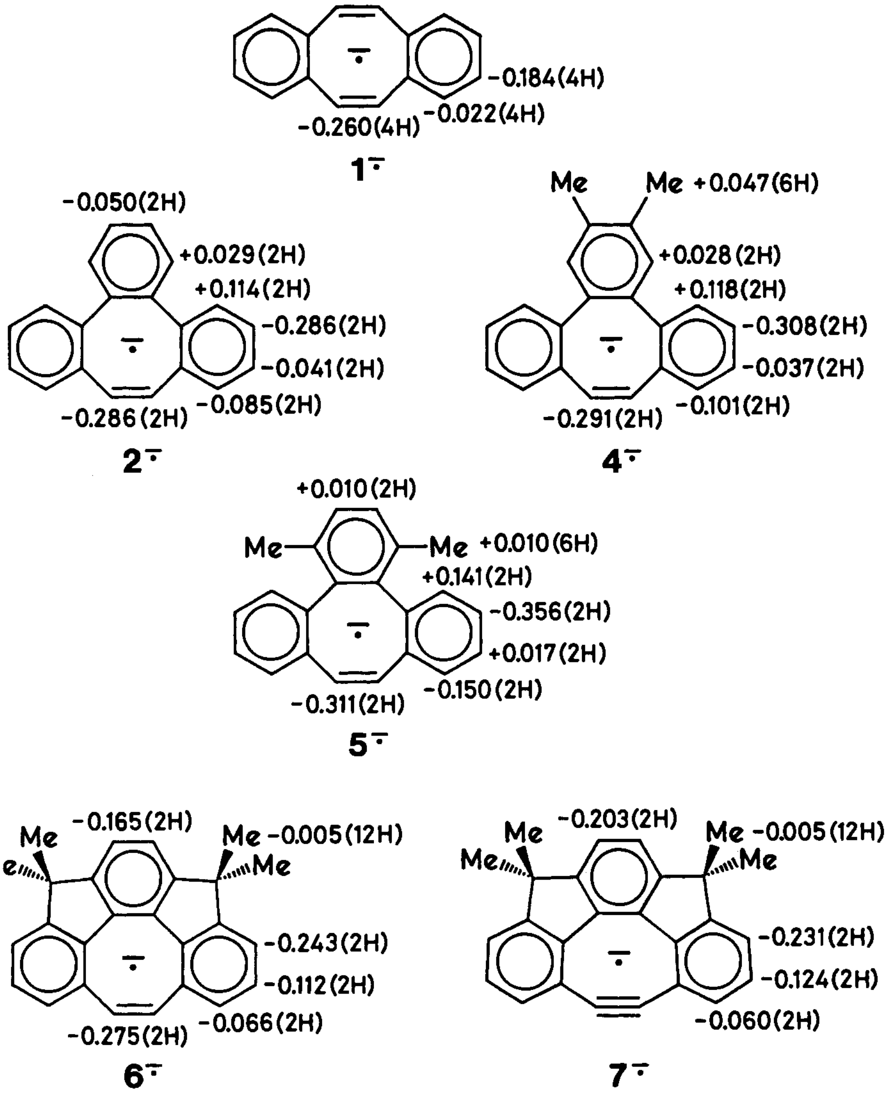


Fig. 4. *Proton-coupling constants,* a_{H_μ} [mT], *for* $\mathbf{1}^{\cdot-}$ ([7]; signs determined in this work), $\mathbf{2}^{\cdot-}$, *and* $\mathbf{4}^{\cdot-}$-$\mathbf{7}^{\cdot-}$. g-Factors: 2.0027 for $\mathbf{1}^{\cdot-}$, $\mathbf{6}^{\cdot-}$, and $\mathbf{7}^{\cdot-}$; 2.0028 for $\mathbf{2}^{\cdot-}$, $\mathbf{4}^{\cdot-}$, and $\mathbf{5}^{\cdot-}$. Exper. error: ±0.002 and ±0.001 mT in $|a_{H_\mu}|$ larger and smaller than 0.2 mT, respectively; ±0.0001 in g.

i) Deuteration at C(9) in **2** *and* **5** *and in the corresponding position of* **6**. The coupling constants of –0.286, –0.311, and –0.275 mT for one α-proton[2]) in $\mathbf{2}^{\cdot-}$, $\mathbf{5}^{\cdot-}$, and $\mathbf{6}^{\cdot-}$ are then replaced by the corresponding deuteron values of –0.044, –0.048, and –0.042 mT, respectively.

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[2]) By convention, protons separated from a π-centre by 0, 1, 2,... sp^3-hybridized C-atom are denoted α, β, γ,... The coupling constant of β-protons in the Me substituent of a radical anion is usually of similar absolute value as that of the replaced α-protons, but of opposite sign [15].

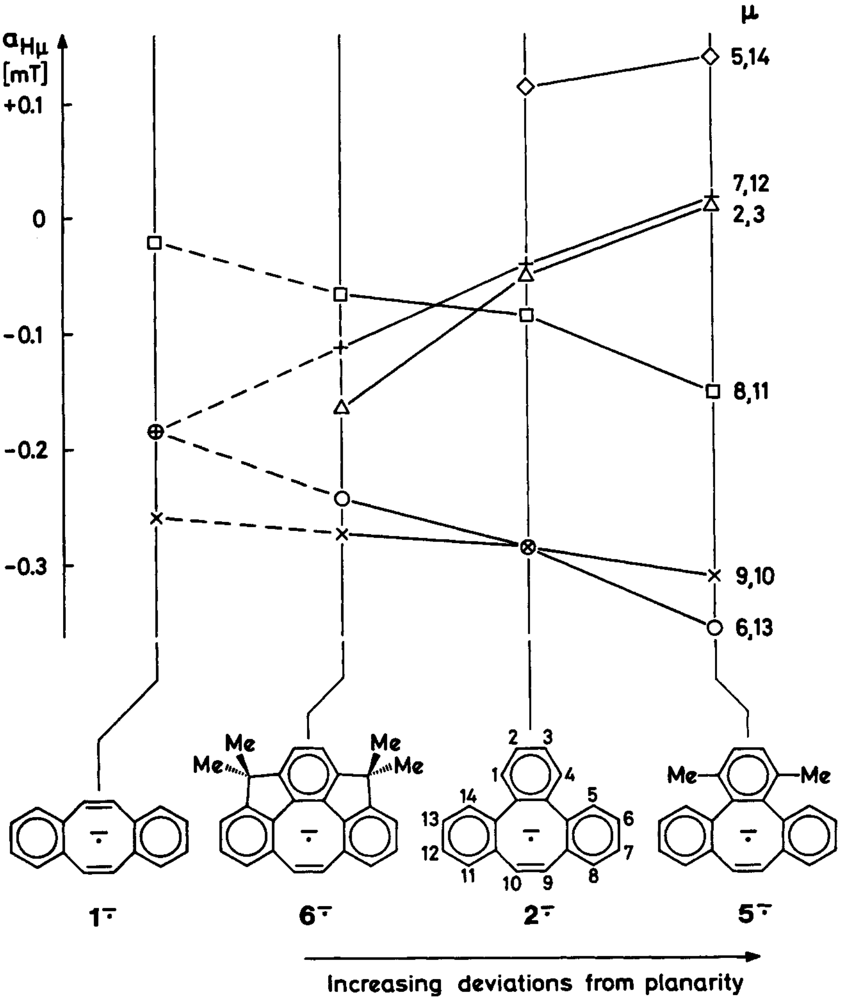


Fig. 5. *Correlation of the α-proton-coupling constants,* $a_{H\mu}$, *for* **1**$^{\overline{\cdot}}$, **2**$^{\overline{\cdot}}$, **5**$^{\overline{\cdot}}$, *and* **6**$^{\overline{\cdot}}$. For the sake of comparison, the numbering of the proton-bearing C-atoms in **1**$^{\overline{\cdot}}$ and **6**$^{\overline{\cdot}}$ is the same as that of the corresponding positions μ in **2**$^{\overline{\cdot}}$ and **5**$^{\overline{\cdot}}$.

ii) Dimethyl substitution in the less sterically hindered 2,3-positions of **2**. The coupling constant of –0.050 mT of the two α-protons in **2**$^{\overline{\cdot}}$ is then replaced by that of +0.047 mT arising from the six methyl β-protons[2]) in **4**$^{\overline{\cdot}}$.

iii) Occurrence of substantial positive coupling constants, +0.114, +0.118, and +0.141 mT, *for* **2**$^{\overline{\cdot}}$, **4**$^{\overline{\cdot}}$, and **5**$^{\overline{\cdot}}$, *respectively*. As values of this sign and magnitude are missing for **6**$^{\overline{\cdot}}$ and **7**$^{\overline{\cdot}}$, they must belong to positions which bear α-protons in **2**$^{\overline{\cdot}}$, **4**$^{\overline{\cdot}}$, and **5**$^{\overline{\cdot}}$, but lack such protons in **6**$^{\overline{\cdot}}$ and **7**$^{\overline{\cdot}}$. These positions are, therefore, 5 and 14.

iv) Calculations of π-spin populations, ρ_μ, *at the centres* μ *by the* Hückel-McLachlan *procedure* ($\lambda = 1.0$) *for simple MO models of tribenzo[*a,c,e*]cyclooctene*. In these models

(*Fig. 6*), the two pairs of essential single bonds, C(8a)–C(9), C(10)–C(10a) and C(4a)–C(4b), C(14a)–C(14b), are accounted for by parameters β' and β'', respectively. In the case of a planar radical anion such as **6**$^{\cdot-}$, a value of 0.8β has been adopted for both parameters. Increasing deviations from planarity on going from **6**$^{\cdot-}$ to **2**$^{\cdot-}$ to **5**$^{\cdot-}$ are simulated by further changing this value for β'' from 0.8 to 0.6 to 0.4β. *Table 2* lists the α-proton-coupling constants, obtained from the calculated π-spin populations ρ_μ with the use of the *McConnell* equation $a_{H_\mu} = Q \cdot \rho_\mu$ [16], in which the conversion factor, $Q = 8\ (-0.321\ \text{mT}) = -2.57\ \text{mT}$ [4b] [5], is the total width of the ESR spectrum of the cyclooctatetraene radical anion. The MO-theoretical coupling constants for $\beta'' = 0.8$, 0.6, and 0.4β fairly match their experimental counterparts for **6**$^{\cdot-}$, **2**$^{\cdot-}$, and **5**$^{\cdot-}$, respectively, as far as the relative absolute values, signs and trends on increasing deviations from planarity are concerned. In general, these deviations lead to a shift of the π-spin populations from the benzene ring Ⓒ to the residual (*Z*)-stilbene-like π-system containing the rings Ⓐ and Ⓑ and the essential double bond C(9)–C(10) (*Fig. 6*).

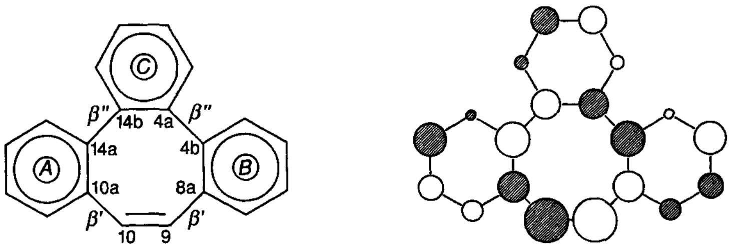


Fig. 6. Hückel *models of tribenzo[*a,c,e*]cyclooctene*. Left: parameters β' and β''; right: diagram of the LUMO for $\beta' = \beta'' = 0.8\beta$.

Table 2. *Comparison of Calculated and Experimental α-Proton-Coupling Constants, a_{H_μ}* [mT], *for* **6**$^{\cdot-}$, **2**$^{\cdot-}$, *and* **5**$^{\cdot-}$

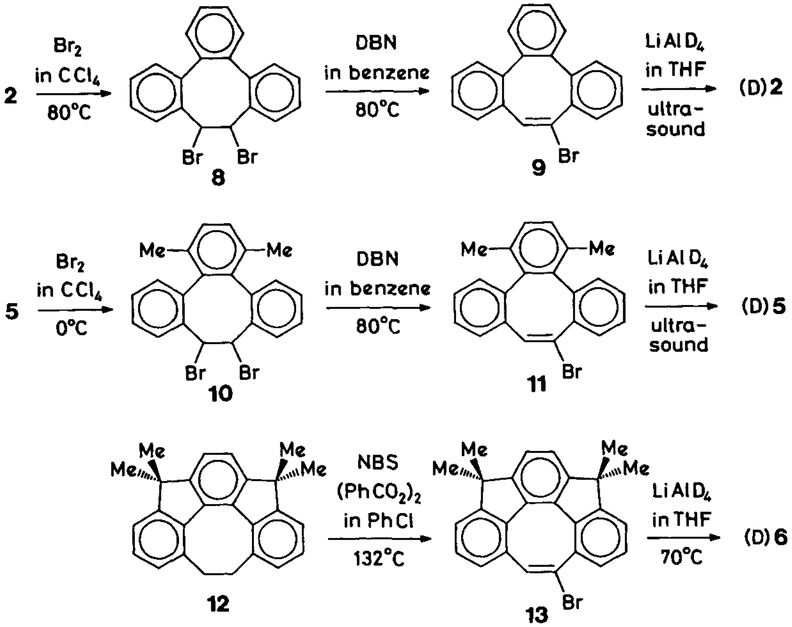
	a_{H_μ}, calc.a)			a_{H_μ}, exp.b)		
μ	$\beta''=0.8\beta$	$\beta''=0.6\beta$	$\beta''=0.4\beta$	**6**$^{\cdot-}$c)	**2**$^{\cdot-}$	**5**$^{\cdot-}$
1,4	+0.005	+0.007	+0.005	d)	+0.029	d)
2,3	–0.093	–0.061	–0.030	–0.165	–0.050	+0.010
5,14	+0.044	+0.067	+0.067	d)	+0.114	+0.141
6,13	–0.175	–0.224	–0.267	–0.243	–0.286	–0.356
7,12	–0.064	–0.021	+0.018	–0.112	–0.041	+0.017
8,11	–0.041	–0.087	–0.139	–0.066	–0.085	–0.150
9,10	–0.406	–0.470	–0.527	–0.275	–0.286	–0.311

a) See text and *Fig. 6*. b) See *Fig. 4*. c) For the sake of comparison, the numbering of the proton-bearing centres μ in **6**$^{\cdot-}$ is the same as that of the corresponding positions in **2**$^{\cdot-}$ and **5**$^{\cdot-}$. d) No α-protons in these positions μ.

Conclusions. – The results presented above bear out the expectation that the radical anions of the 'bridged' tribenzocyclooctenes **6** and **7** are planar, whereas those of the 'unbridged' or dimethyl substituted compounds **2**, **4**, and **5** are not. Deviations from planarity increase in the order $\mathbf{6}^{\cdot-}, \mathbf{7}^{\cdot-} < \mathbf{2}^{\cdot-}, \mathbf{4}^{\cdot-} < \mathbf{5}^{\cdot-}$. The MO models are consistent with steric hindrance in the *peri*-positions 1↔14 and 4↔5 being mainly alleviated by a twist about the essential single bonds C(4a)–C(4b) and C(14a)–C(14b).

Experimental. – *Syntheses.* Those of **2** [17], **5** [9] [10], **6** [10], and **7** [12] have been described previously. The compound **4** was prepared by *Diels-Alder* cycloaddition of 2,3-dimethylbuta-1,3-diene to 5,6-didehydro-[*a,e*]cyclooctene [18] and subsequent oxidation of the product with 2,3-dichloro-5,6-dicyanobenzo-1,4-quinone. The deuterated derivatives (D)**2**, (D)**5**, and (D)**6** were synthesized as indicated in the *Scheme*.

Scheme



Accordingly, **2** underwent bromination to yield **8** [19] which was dehydrobrominated with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) to give **9**. The bromide **9** was reduced with $LiAlD_4$ under ultrasound sonification to provide (D)**2**. By an analogous procedure, **5** was converted into (D)**5** *via* **10** and **11**. The synthesis of (D)**6** started with the dihydro-precursor **12** [10]. Treatment of **12** with *N*-bromosuccinimid (NBS) and benzoyl-peroxide afforded the bromide **13** which was reduced with $LiAlD_4$ to (D)**6**.

Instrumental. The ESR spectra were taken on a *Varian-E9*-spectrometer, while a *Bruker-ESP-300*-spectrometer system served for ENDOR and TRIPLE-resonance studies.

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