Dibenzo[*a,e*]cyclooctene: a Nonplanar Radical Cation

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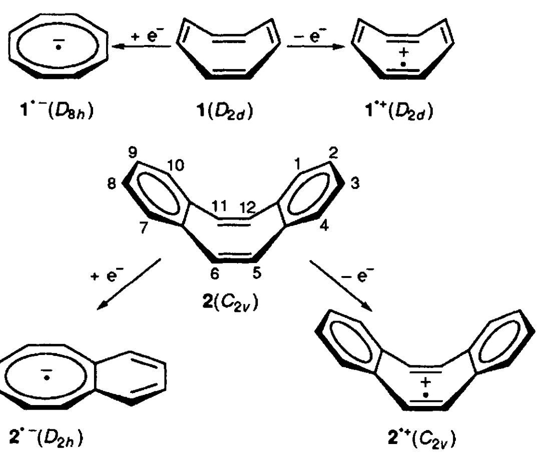
Upon oxidation to the radical cation, the eight-membered ring in dibenzo[*a,e*]cyclooctene (**2**) seems to retain its tub-shaped geometry; in this regard, **2** resembles the parent cyclooctatetraene **1**.

Cyclooctatetraene **1** has a tub-shaped carbon framework,[1] whereas in both the dianion $\mathbf{1}^{2-}$ and the radical anion $\mathbf{1}^{\cdot -}$ the π-perimeter appears to be flattened.[2] The coupling constant, $|a_H|$ 0.321 mT, of eight equivalent ring protons in $\mathbf{1}^{\cdot -}$ is fully consistent with the planar geometry. In contrast, the radical cation $\mathbf{1}^{\cdot +}$, generated from **1** with Co^{3+} ion in trifluoroacetic acid using a flow system, must be tub-shaped like its neutral precursor, because the corresponding coupling constant $|a_H|$ is only 0.15 mT.[3] It is well known that deviations of the π-system from the planarity cause a decrease in the $|a_H|$ values of protons attached to this system (α-protons), as the positive contributions by π,σ-spin delocalization partially cancel the negative ones due to π,σ-spin polarization.[4] Very recently, an X-ray crystallographic structure analysis was reported for a salt of the tetrakis(bicyclo[2.2.2]octeno)cyclooctatetraene radical cation,[5] in which the π-system of **1** is embedded in a bulky carbon framework. The eight-membered ring in this radical cation, like that in the corresponding neutral molecule,[6] has a tub shape; its flattening, however, may be disfavoured by the four annelated bicyclic moieties. On the other hand, dibenzo[*a,e*]cyclooctene **2** shares the tub-shaped eight-membered ring with the parent **1**,[7] although its planar geometry is not sterically hindered by the two annelated benzenes. Electrochemical and EPR studies strongly suggest that this ring is essentially flattened in the radical anion $\mathbf{2}^{\cdot -}$,[8,9] as it is in $\mathbf{1}^{\cdot -}$. The results of the present communication indicate that, likewise, the radical cation $\mathbf{2}^{\cdot +}$ resembles $\mathbf{1}^{\cdot +}$ in its geometry, *i.e.* $\mathbf{2}^{\cdot +}$ is also nonplanar.

Table 1 Coupling constants, a_H in mT, and g factors for the radical ions of dibenzo[*a,e*]cyclooctene **2**

	Position	$\mathbf{2}^{\cdot -a,c}$	$\mathbf{2}^{\cdot +b,c}$
a_H	1, 4, 7, 10	(+)0.022	<0.015
	2, 3, 8, 9	(−)0.184	(−)0.161
	5, 6, 11, 12	(−)0.260	(−)0.119
g^d		2.0028	2.0026

[a] Ref. 9; experimental error in $|a_H|$: ±1%. [b] This work; experimental error in $|a_H|$: ±2%. [c] Signs of a_H as required by theory. [d] Experimental error in g: ±0.0001



The radical cation $\mathbf{2}^{\cdot +}$ was generated by UV-irradiation (365 nm) at 250 K in a stationary system which consisted of a solution of **2** in a 2:5 dichloromethane–trifluoroacetic acid mixture containing the Hg^{2+} ion.[10] The EPR spectrum of the short-lived $\mathbf{2}^{\cdot +}$ thus formed (half-life *ca.* 15 min) is shown in Fig. 1. Its hyperfine pattern arises from two sets of four protons with $|a_H|$ 0.161 and 0.119 mT; a splitting from the third

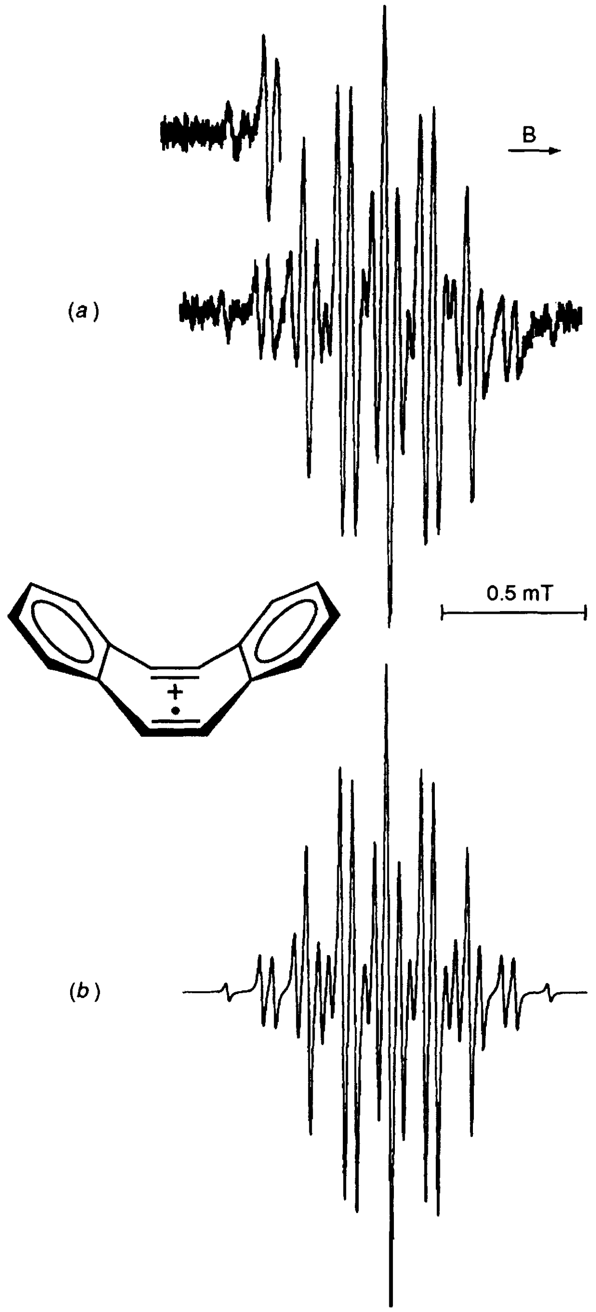


Fig. 1 (*a*) EPR spectrum of $\mathbf{2}^{\cdot +}$. Solvent CH_2Cl_2/CF_3CO_2H (2:5), counterion $CF_3CO_2^-$, temperature 250 K. (*b*) Simulation with the use of the coupling constants in Table 1; line-shape Lorentzian, line-width 0.025 mT.

set of four protons is smaller than 0.015 mT and remains unresolved. In Table 1, these values are compared with the corresponding data for $\mathbf{2}^{\cdot -}$.[9] Assignment of $|a_{\mathrm{H}}|$ 0.119 mT to the 5,6,11,12-protons is based on the EPR spectrum of the radical cation deuteriated in these positions,† because the pertinent coupling constant $|a_{\mathrm{H}}|$ was replaced in it by the corresponding splitting ($|a_{\mathrm{D}}|$ 0.018 mT) from four deuterons. The ratio $|a_{\mathrm{H}}|\,(\mathbf{2}^{\cdot +})/|a_{\mathrm{H}}|(\mathbf{2}^{\cdot -}) = 0.119\ \mathrm{mT}/0.260\ \mathrm{mT} = 0.46$ for the four protons at the eight-membered ring of dibenzo[*a*,*e*]cyclooctene is equal to the corresponding ratio $|a_{\mathrm{H}}|(\mathbf{1}^{\cdot +})/|a_{\mathrm{H}}|(\mathbf{1}^{\cdot -}) = 0.15\ \mathrm{mT}/0.321\ \mathrm{mT}$ for the eight protons of the parent cyclooctatetraene. It has been shown[11] that 'similar deviations of the π-system from the planarity have similar effects on the α-proton coupling constants provided that the singly occupied orbitals of the radical are interrelated'. This is here certainly the case. Taking the radical anions $\mathbf{1}^{\cdot -}$ and $\mathbf{2}^{\cdot -}$ as the planar reference π-systems, one thus concludes that the radical cations $\mathbf{1}^{\cdot +}$ and $\mathbf{2}^{\cdot +}$ must resemble each other in the tub-shaped geometry of their eight-membered rings.

The coupling constants of the α-protons at the benzene rings in $\mathbf{2}^{\cdot +}$ are less affected by the nonplanarity than those at the 5–6 and 11–12 'double' bonds (Table 1). A similar observation was made for the radical anion of the structurally related (*Z*)-stilbene which deviates more strongly from the planarity than that of the (*E*)-isomer. On passing from the latter to the former, the $|a_{\mathrm{H}}|$ value of the protons at the central double bond decreases from 0.449 to 0.268 mT, whereas those of the phenyl protons hardly change.[12]

We thank Dr Qian Wang, now in Gif/Yvette, France, for assistance in the synthesis of 5,6,11,12-tetradeuteriodibenzo[*a*,*e*]cyclooctene. This work was supported by Swiss National Science Foundation.

Received, 7th March 1994; Com. 4/01349B

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† The preparation of the 5,6,11,12-tetradeuteriodibenzo[*a*,*e*]cyclooctene followed the procedure described in ref. 9. According to NMR and MS, the deuterium content of the product was *ca*. 75%.

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