

133. The Radical Anions of Some Benzo-Derivatives of Dehydrocyclooctatetraenes

by Fabian Gerson and René Heckendorf

Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

and Henry N.C. Wong¹⁾

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

In memory of Professor Franz Sondheimer

(6. V. 83)

Summary

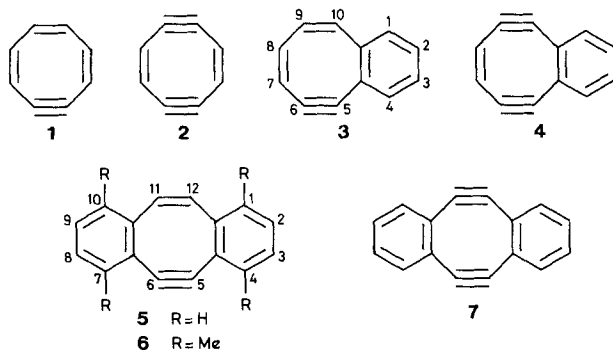
The radical anions of 5,6-didehydrobenzocyclooctene (3), 5,6,9,10-tetrahydrobenzocyclooctene (4) and 1,4,7,10-tetramethyl-5,6-didehydridibenzo[*a, e*]cyclooctene (6) were prepared *in situ* from dibromo-precursors and have been characterized by ESR and ENDOR spectroscopy.

Introduction. – Dehydrocyclooctatetraenes and their benzo-derivatives have received much attention in the last few years [1]. Insertion of a triple bond into the unsaturated eight-membered ring increases its tendency to flatten; concurrently, the propensity of the hydrocarbon to undergo addition, dimerization and rearrangement reactions is enhanced. The reactivity is, in general, lowered by introducing a second triple bond and by fusing benzene rings to the dehydrocyclooctatetraene π -system [1].

The transient existence of cyclooctatrienyne (1), the simplest member of the series, has been proved by trapping 1 with various reagents [2]. Attempts to synthesize cycloocta-1,5-diene-3,7-diyne (2) [3] and 5,6-didehydrobenzocyclooctene (3) [4] have failed so far, while 5,6,9,10-tetrahydrobenzocyclooctene (4) was obtained as a rapidly decomposing oil [5]. 5,6-Didehydridibenzo[*a, e*]cyclooctene (5) and 5,6,11,12-tetrahydridibenzo[*a, e*]cyclooctene (7) were both isolated in crystalline form [6], but only the diyne 7 is relatively stable at room temperature. In addition to 5, its 1,4,7,10-tetramethyl derivative (6) has quite recently been prepared [7]. It is noteworthy that the first synthesis claimed for 6 [8] yielded, in fact, the isomeric 1,4,6,9-tetramethylbenzo[*b*]biphenylene [9].

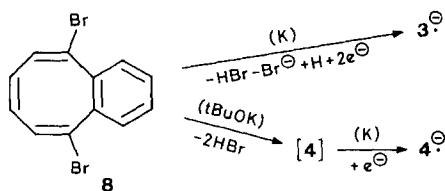
The radical anions 1^{\ominus} [10], 5^{\ominus} [11] and 7^{\ominus} [11] have been characterized by ESR spectroscopy; the hyperfine data are consistent with a planar eight-membered

¹⁾ Also spelled as *Nai Zheng Huang*.



ring [11] [12]. It has been found that isolation of the neutral dehydrocyclooctatetraenes is not required for preparation of their radical anions which can be obtained *in situ* from bromo-precursors. For instance, 1^{\ominus} was generated by reacting bromocyclooctatetraene with potassium metal in a mixture of tetrahydrofuran (THF) and hexamethylphosphoric acid triamide (HMPT) at 173 K [10]. Thus, it is possible to investigate the radical anion of a dehydrocyclooctatetraene in solution, even if the neutral compound is too reactive to be isolated. The present work describes ESR and ENDOR studies of 3^{\ominus} , 4^{\ominus} and 6^{\ominus} which have been prepared directly from dibromo-precursors.

Results and Discussion. – *Radical anions of 5,6-didehydro- (3) and 5,6,9,10-tetrahydrobenzocyclooctene (4).* Reaction of 5,10-dibromobenzocyclooctene (**8**) [5] with potassium metal in a 10:1 mixture of THF and HMPT at 173 K led to a paramagnetic species which gave rise to the ESR and ENDOR spectra shown in *Figure 1* ($g = 2.0026 \pm 0.0001$). On the other hand, dehydrobromination of **8** with *t*-BuOK in 1,2-dimethoxyethane (DME) at 193 K, followed by reduction *in situ* with potassium metal at the same temperature, afforded a different paramagnetic species which exhibited the ESR and ENDOR spectra reproduced in *Figure 2* ($g = 2.0026 \pm 0.0001$). The hyperfine data for the two species (*Table 1*) clearly identify them as the radical anions of the elusive monoynone **3** (*Fig. 1*) and the unstable diyne **4** (*Fig. 2*). Evidently, in the reaction of **8** with potassium metal to yield 3^{\ominus} , only one HBr molecule was lost, whereas the second Br-atom (presumably leaving as the anion Br^{\ominus}) was replaced by a H-atom abstracted from the solvent. By contrast, in the treatment of **8** with *t*-BuOK, two HBr molecules were eliminated to form **4** which was subsequently reduced to 4^{\ominus} .



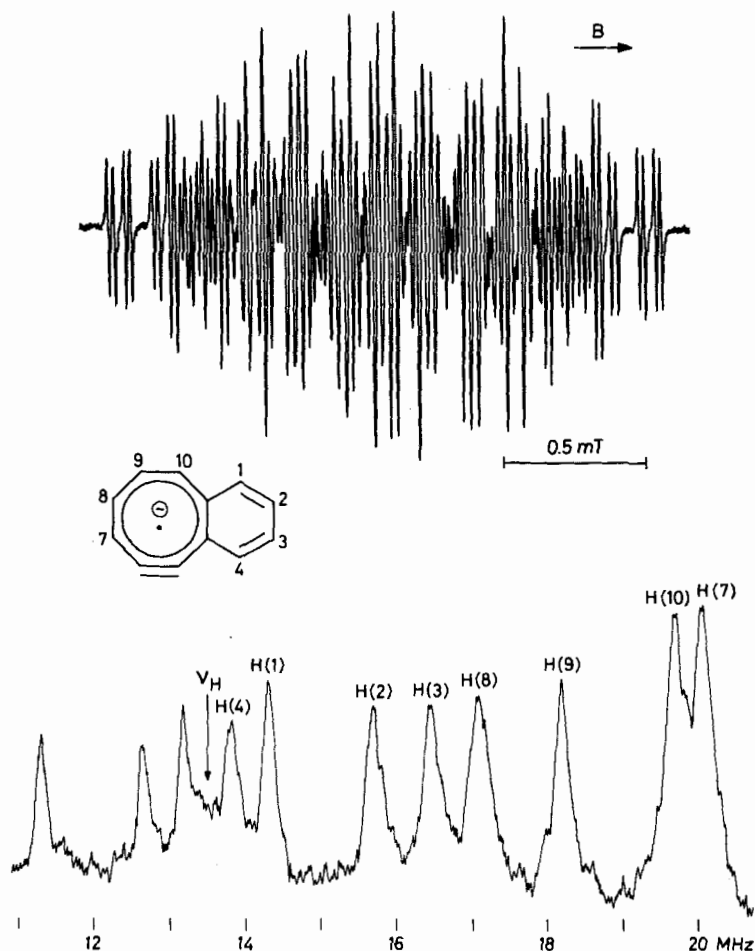


Fig. 1. ESR (top) and proton ENDOR spectra (bottom) of the radical anion of 5,6-didehydrobenzocyclooctene (3). Solvent: THF/HMPT (10:1); counterion: K^{\oplus} ; temp.: 173 K. ν_H = frequency of the free proton.

Table 1. Proton coupling constants (in mT^a) for the radical anions of 5,6-didehydro- (3) and 5,6,9,10-tetrahydrobenzocyclooctene (4)

Position	3 [⊖]	4 [⊖]	Position	3 [⊖]	4 [⊖]
1	0.057 (1 H)	0.031 (2 H)	7	0.464 (1 H)	0.473 (2 H)
4	0.021 (1 H)		8	0.256 (1 H)	
2	0.155 (1 H)	0.189 (2 H)	9	0.335 (1 H)	-
3	0.212 (1 H)		10	0.435 (1 H)	-

^a) Experimental error: ± 0.001 mT

Upon prolonged contact of the solution of 3^{\ominus} in THF/HMPT, the ESR spectrum of this radical anion disappeared and, shortly after, was replaced by the well-known spectrum of the isomeric radical anion of biphenylene [13].

There is a general agreement between the observed proton coupling constants and the values calculated for planar radical anions 3^{\ominus} and 4^{\ominus} with the use of MO models which are analogous to those successfully applied to 5^{\ominus} and 7^{\ominus} in a previous work [11]. This agreement bears out the expectation that the eight-membered ring in 3^{\ominus} and 4^{\ominus} is essentially planar.

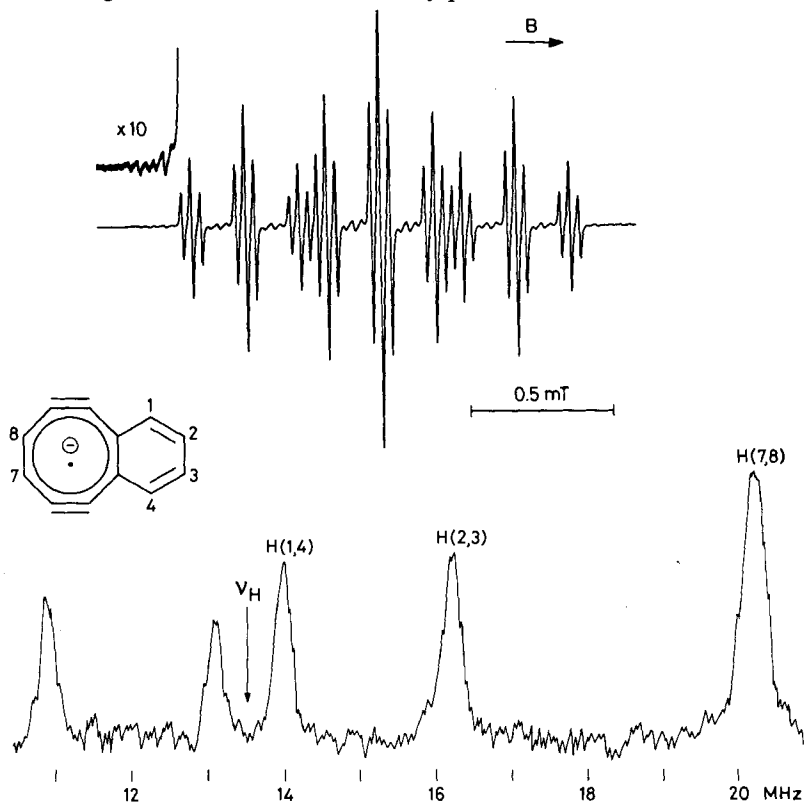


Fig. 2. ESR (top) and proton ENDOR spectra (bottom) of the radical anion of 5,6,9,10-tetrahydrobenzo-cyclooctene (**4**). Solvent: DME; counterion: K^{\oplus} ; temp.: 193 K. The inset at the low-field part of the ESR spectrum shows amplified ^{13}C -satellite lines. ν_H = frequency of the free proton.

Since no deuterated derivatives are available, assignments of the proton hyperfine data have been based on correlation of these data with their MO theoretical counterparts. Whereas the three coupling constants found for 4^{\ominus} can, in this way, be unambiguously assigned to the three pairs of equivalent protons (Fig. 2 and Table 1), the procedure is less straightforward in the case of the eight coupling constants obtained for 3^{\ominus} , and consequently, their assignments to the eight single protons (Fig. 1 and Table 1) are subject to some uncertainty. This statement holds, in particular, for the four larger values which, according to all MO models of 3^{\ominus} ,

should be attributed to the four protons in the eight-membered ring. It is possible that the coupling constants assigned to the protons in the positions 7 and 10 have to be exchanged; neither can an alternative assignment be excluded for the coupling constants of the protons in the positions 8 and 9.

For 4^{\ominus} , ^{13}C -satellite lines (Fig. 2, inset) were analyzed, in addition to the proton hyperfine pattern. The analysis yielded two coupling constants of 0.37 and 0.20 ± 0.01 mT, each for ^{13}C -nuclei in two equivalent C-sites, and 0.14 ± 0.02 mT for such isotopes in four C-sites. While the largest value can, with some confidence, be attributed to ^{13}C -nuclei in the positions 7 and 8, reliable assignments of the remaining coupling constants are rather difficult.

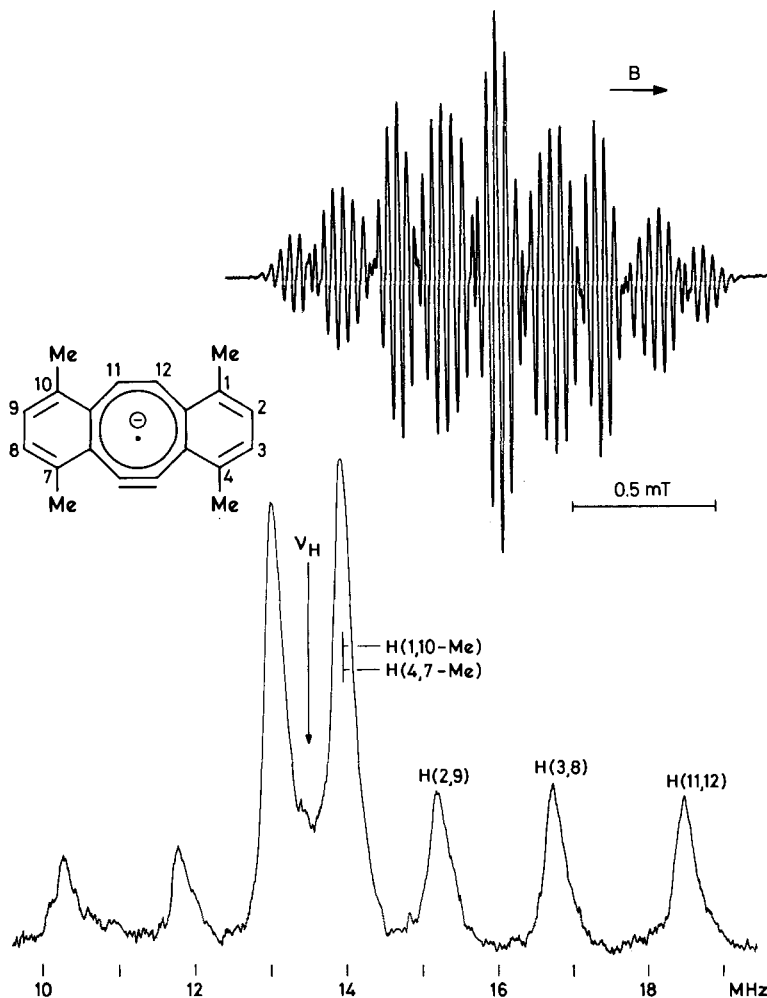


Fig. 3. ESR (top) and proton ENDOR spectra (bottom) of the radical anion of 1,4,7,10-tetramethyl-5,6-didehydrodibenzo[a,e]cyclooctene (6). Solvent: DME; counterion: K^{\oplus} ; temp.: 193 K. ν_H = frequency of the free proton.

Radical anion of 1,4,7,10-tetramethyl-5,6-didehydrodibenzo [a,e]cyclooctene (**6**). Dehydrobromination of 1,4,7,10-tetramethyl-5,6-dibromo-5,6-dihydrodibenzo [a,e]cyclooctene (**9**) with *t*-BuOK in DME at 193 K, followed by reduction *in situ* with potassium metal, produced the paramagnetic species characterized by the ESR and ENDOR spectra in Figure 3 ($g = 2.0026 \pm 0.0001$). Since the pertinent hyperfine data (Table 2) resemble those for the radical anion of unsubstituted 5,6-

Table 2. Proton coupling constants (in mT^a) for the radical anion of 1,4,6,10-tetramethyl-5,6-didehydrodibenzo [a,e]cyclooctene (**6**), as compared with those for the radical anion of the unsubstituted compound (**5**)

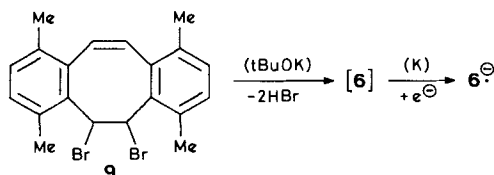
Position	6 [⊖]	5 [⊖] ^{b)}	Position	6 [⊖]	5 [⊖] ^{b)}
1,10	0.033 (6 H ^c)	0.004 (2 H)	4,7	0.033 (6 H ^c)	0.040 (2 H)
2,9	0.120 (2 H)	0.159 (2 H)	11,12	0.348 (2 H)	0.336 (2 H)
3,8	0.227 (2 H)	0.217 (2 H)			

a) Experimental error: ± 0.001 mT.

b) Taken from [11]; solvent DME.

c) Protons of two methyl substituents.

didehydrodibenzo [a,e]cyclooctene (**5**) [11], the paramagnetic species is undoubtedly the radical anion of the unrearranged tetramethyl derivative **6**.



Isomerization of **6**[⊖] to the radical anion of 1,4,6,9-tetramethylbenzo [b]phenylene was not observed upon prolonged contact with the potassium mirror, in contrast to the behaviour of **3**[⊖] under analogous conditions (see above).

The similarity of the proton coupling constants for **5**[⊖] and **6**[⊖] suggests that the structures of the two radical anions are not greatly different. In particular, it is reasonable to assume that the eight-membered ring (which is considered to be planar in **5**[⊖] [11] [12]) does not appreciably pucker in **6**[⊖], although the tetramethyl substitution should markedly increase the steric hindrance of planarity.

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