

218. Rearrangement of the Radical Anions of 1,6-Bridged [10]Annulenes to Derivatives of 5*H*-Benzocycloheptene and Benzotropylium

by Fabian Gerson and Walter Huber

Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland
and Klaus Müllen

Organisch-Chemisches Institut der Universität Köln, Greinstrasse 4, D-5000 Köln 41, Germany

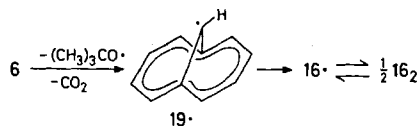
Herrn Professor Dr. *Edgardo Giovannini* zu seinem 70. Geburtstag gewidmet

(29.VI.79)

Summary

The rearrangement products obtained upon reduction of 1,6-methano[10]-annulene (**1**) and its 11-halogen derivatives have been studied by ESR. and, in part, by ENDOR. spectroscopy. These derivatives comprise 11,11-difluoro- (**2**), 11-fluoro- (**3**), 11,11-dichloro- (**4**) and 11-bromo-1,6-methano[10]annulene (**5**), as well as the 2,5,7,10-tetradeuteriated compounds **2-D₄** and **3-D₄**. The studies of the secondary products in question have been initiated by the finding that the radical anion of 11,11-dimethyltricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene (**12**), *i.e.*, the prevailing valence isomer of 11,11-dimethyl-1,6-methano[10]annulene, undergoes above 163 K a rearrangement to the radical anion of 5,5-dimethylbenzocycloheptene (**14**). A rearrangement of this kind also occurs for the radical anion of the parent compound **1**, albeit only above 323 K. The lower reactivity of **1[⊖]** relative to **12[⊖]** is rationalized by the assumption that the first and rate determining step in the case of **1[⊖]** is the valence isomerization to the radical anion of tricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene (**1a**). In the reducing medium used in such reactions (potassium in 1,2-dimethoxyethane), the final paramagnetic product of **1[⊖]** is not 5*H*-benzocycloheptene (**15**), but the benzotropylium radical dianion (**16[⊖]**). This product (**16[⊖]**) is also obtained from the radical anions of the halogen-substituted 1,6-methano[10]annulenes, **2** to **5**, in the same medium. The temperatures required for the conversion of **2[⊖]** and **3[⊖]** into **16[⊖]** lie above 293 and 243 K, respectively, whereas the short-lived species **4[⊖]** and **5[⊖]** undergo such a rearrangement already at 163 K. The stability of the four halogen-substituted radical anions thus decreases in the sequence **2[⊖]** > **3[⊖]** > **4[⊖]** ≈ **5[⊖]**. Replacement of **2[⊖]** and **3[⊖]** by **2-D₄[⊖]** and **3-D₄[⊖]**, respectively, leads to 1,4,5,8-tetradeuteriobenzotropylium radical dianion (**16-D₄[⊖]**). Experimental evidence and theoretical arguments indicate that the rearrangements in question are initiated by a loss of one (**3[⊖]** and **5[⊖]**) or two (**2[⊖]** and **4[⊖]**) halogen atoms. Such a reaction step must involve the intermediacy of the radical **19[·]** (see below) which rapidly isomerizes to the benzotropylium

radical **16** \cdot . Support for the transient existence of **19** \cdot is provided by the thermolysis of 1,6-methano[10]annulene-11-*t*-butylperoxyester (**6**) which yields **16** \cdot in a temperature dependent equilibrium with a mixture of its dimers (**16**₂).



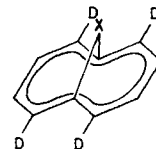
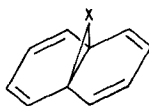
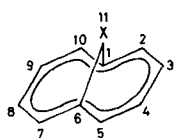
In the hitherto unreported ESR. spectra of **2** \ominus and **3** \ominus , the coupling constants of the ring protons differ considerably from the analogous values for the radical anions of other 1,6-bridged [10]annulenes. These differences strongly suggest that the fluoro-substitution substantially affects the character of the singly occupied orbital.

Introduction. - The radical anions of 1,6-methano[10]annulene (**1**) and their heteroanalogues, 1,6-imino- (**9**), 1,6-methylimino- (**10**) and 1,6-oxido[10]annulene (**11**), have been extensively studied by ESR. spectroscopy [1-3]. These studies also included the radical anions of the corresponding 2,5,7,10-tetradeuterio-derivatives, **1-D**₄, **9-D**₄, **10-D**₄ and **11-D**₄.

The stabilities of the four radical anions have been found to decrease in the order **1** \ominus \gg **9** \ominus $>$ **11** \ominus $>$ **10** \ominus [2]. Whereas, at 193 K, the ESR. spectrum of **1** \ominus remained unchanged for weeks, those of **9** \ominus , **11** \ominus and **10** \ominus diminished in intensity, according to half-lives of 60, 15 and 2 min, respectively. Renewed reduction, following the disappearance of these spectra, led to the ESR. signals of the radical anion of naphthalene, except for **10** \ominus which under certain conditions yielded the radical anion of azulene. With the use of **9-D**₄, **10-D**₄ and **11-D**₄ as the starting material, the analogous secondary products were the radical anion of 1,4,5,8-tetradeuterionaphthalene, or alternatively, in the case of **10-D**₄, that of 1,4,5,8-tetradeuterioazulene (the latter containing *ca.* 30% of the 1,5,8-trideuterio-derivative) [1] [2].

More recently [4], it has been observed that the radical anion of 11,11-dimethyltricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene (**12**) readily undergoes a rearrangement to the radical anion of 5,5-dimethylcycloheptene (**14**). The compound **12** represents a valence isomer of 11,11-dimethyl-1,6-methano[10]annulene which, in contrast to parent compound **1**, exists preferentially in a tricyclic 'bisnorcaradiene' form with a C(1),C(6)-bond. Thus, an obvious question is whether a rearrangement analogous to **12** \ominus \rightarrow **14** \ominus also occurs with **1** \ominus under more rigorous conditions, *i.e.*, whether **1** \ominus can be converted to the radical anion of 5-*H*-benzocycloheptene (**15**). In addition, one may inquire into the behaviour of the radical anions produced from those halogen-derivatives of **1** which, like **12**, are substituted at the bridging C-atom, but which possess an 'open' [10]annulene structure. To this end, we have investigated the hitherto unknown radical anions of 11,11-difluoro- (**2**), 11-fluoro- (**3**), 11,11-dichloro- (**4**) and 11-bromo-1,6-methano[10]annulene (**5**), as well as those of the 2,5,7,10-tetradeuterio-derivatives of **2** (**2-D**₄) and **3** (**3-D**₄). Apart from studying the structure and reactivity of these radical anions, we have examined the products obtained by photolysis and thermolysis of the neutral 1,6-

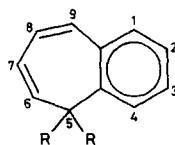
methano[10]annulene-11-*t*-butylperoxyester (6). As will be shown below, the rearrangements observed in the present work involve the formation of the benzotropylium system (16) or, respectively, its 1,4,5,8-tetradeuterio-derivative (16-D₄).



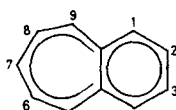
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|---|----------------------------|
| 1 X = >CH ₂ | 7 X = >CHCO ₂ H |
| 2 X = >CF ₂ | 8 X = >CO |
| 3 X = >CHF | 9 X = >NH |
| 4 X = >CCl ₂ | 10 X = >NCH ₃ |
| 5 X = >CHBr | 11 X = >O |
| 6 X = >CHCO ₃ C(CH ₃) ₃ | |

- | |
|--|
| 12 X = >C(CH ₃) ₂ |
| 13 X = $\begin{cases} -\text{CH}_2 \\ -\text{CH}_2 \end{cases} \text{O}$ |

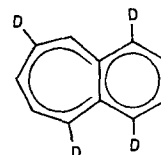
- | |
|---|
| 1-D ₄ X = >CH ₂ |
| 2-D ₄ X = >CF ₂ |
| 3-D ₄ X = >CHF |
| 9-D ₄ X = >NH |
| 10-D ₄ X = >NCH ₃ |
| 11-D ₄ X = >O |



- 14 R = CH₃
15 R = H



16



16-D₄

Experimental Part. - The syntheses of 11,11-difluoro-1,6-methano[10]annulene (2), 11-fluoro-1,6-methano[10]annulene (3), 11,11-dichloro-1,6-methano[10]annulene (4), 11-bromo-1,6-methano[10]annulene (5) and 11,11-dimethyltricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene (12) have been described elsewhere (2: [5-7]; 3: [5] [8]; 4: [6] [9]; 5: [10] [11]; 12: [12] [13]).

The syntheses of 1,6-methano[10]annulene-11-carboxylic acid (7) and 11-oxo-1,6-methano[10]annulene (8) are also known [11] (the hyperfine data for the radical anions of 7 and 8 will be presented in this paper for the first time).

1,6-Methano[10]annulene-11-*t*-butylperoxyester (6) was prepared in the conventional way by reacting 1,6-methano[10]annulene-11-carboxylic acid chloride (available from the acid 7) with *t*-butylhydroperoxide.

5,5-Dimethylbenzocycloheptene (14) was yielded by thermolysis of 12 [4] [13].

2,5,7,10-Tetradeuterio-11,11-difluoro-1,6-methano[10]annulene (2-D₄) and 2,5,7,10-tetradeuterio-11-fluoro-1,6-methano[10]annulene (3-D₄) were obtained from the respective parent compounds 2 and 3 by an isotope exchange in perdeuteriodimethylsulfoxide with the use of potassium-*t*-butylate as a base. Experimental details for analogous deuteration of 1,6-oxido[10]annulene (11) have been given in a previous paper [1]. The isotopic purity achieved by this method for 2-D₄ and 3-D₄ was 95%, as verified by ¹H-NMR, and mass spectroscopy.

The radical anions were generated both by electrolytic and chemical reduction of the corresponding neutral compounds. The electrolysis was carried out in a cylindrical cell constructed in the Basel laboratory [14]. In general, 1,2-dimethoxyethane (DME) and tetrabutylammonium perchlorate served as the solvent and the supporting salt, respectively, but in some cases *N,N*-dimethylformamide (DMF) and tetraethylammonium salt were used as well. Chemical reduction signified reaction of the neutral compounds with potassium in DME, either by a direct contact of the solution with the metallic mirror or by the indirect method of solvated electrons [15]. In a few experiments DME was replaced by 2-methyltetrahydrofuran (MTHF).

ENDOR spectra could be observed only for the chemically produced radicals, provided that they were present in sufficient concentration at low temperature. This was the case with some secondary products, namely the radical anion of 5,5-dimethylbenzocycloheptene (15), the benzotropylium

radical dianion (16^{\ominus}) and its 1,4,5,8-tetradeuterio-derivative (16-D_4^{\ominus}). The ENDOR instrument was a Varian-1700-system coupled to a Varian-E-9-spectrometer.

Results. - *11,11-Dimethyltricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene* (**12**). The radical anion 12^{\ominus} was relatively short-lived and could be characterized only under special conditions such as very low temperatures and solvents favourable to ion pairing. Figure 1 shows an ESR spectrum of 12^{\ominus} , taken at 153 K with the solvent MTHF and the counter-ion K^{\oplus} . The pertinent coupling constants, $a_{H^{\mu}}$ of the protons are given in Table 1, along with the data for the radical anion of the structurally related *cis*-9,10-(2-oxa-propano)-9,10-dihydronaphthalene (**13**) [1]. The assignment of the values 0.416 ($a_{H(2,5,7,10)}$) and 0.175 mT ($a_{H(3,4,8,9)}$) for 12^{\ominus} is analogous to that made previously for 13^{\ominus} . It follows from comparison with the proton coupling constants found for the radical anion of *trans*-1,3-butadiene [16]

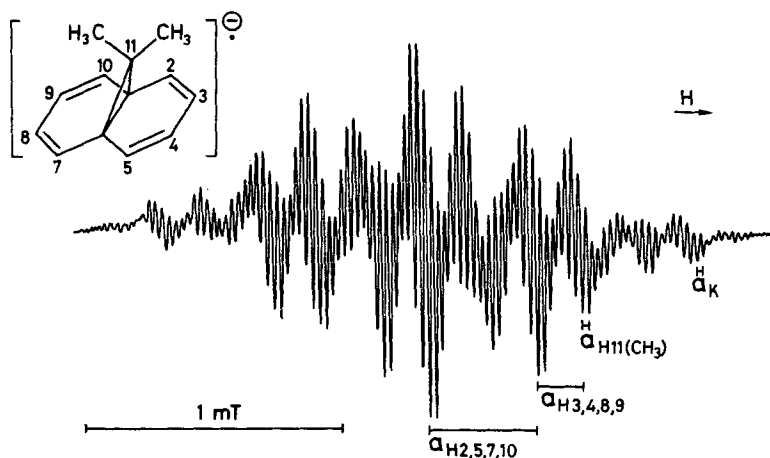


Fig. 1. ESR spectrum of the radical anion of *11,11-dimethyltricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene* (**12**). Solvent: MTHF; counter-ion: K^{\oplus} ; temp.: 153 K.

Table 1. Coupling constants (in mT^a) for the radical anions of *11,11-dimethyltricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene* (**12**) and *cis*-9,10-(2-oxa-propano)-9,10-dihydronaphthalene (**13**)^b

Radical anion	12^{\ominus}	13^{\ominus}
Solvent/ counterion	MTHF/ K^{\oplus}	DME/ K^{\oplus}
Temp. (K)	153	203
$\mu = 2,5,7,10$	0.416 (4H)	0.380 (4H)
3,4,8,9	0.175 (4H)	0.151 (4H)
11	0.025 (6H ^c)	0.045 (4H ^d)

a) Experimental error ± 0.001 and ± 0.002 mT for coupling constants smaller and larger, respectively, than 0.1 mT.

b) Ref. [1].

c) Protons of two methyl groups.

d) Protons of two methylene groups.

(see Discussion). In addition to the coupling constants $a_{H\mu}$, the ESR. spectrum of 12^\ominus (Fig. 1) exhibited a hyperfine splitting $a_K = 0.022$ mT from the ^{39}K -nucleus of the counter-ion.

At temperatures above 163 K, the original spectrum (Fig. 1) was gradually replaced by the one shown in Figure 2. The radical anion giving rise to it has been readily identified as that of 5,5-dimethylbenzocycloheptene (**14**), since the same spectrum was obtained upon reduction of **14** with potassium in MTHF. The analysis of this complex spectrum provides a further example illustrating the potential of the ENDOR. technique, as the coupling constants of the eight single ring protons and the six equivalent methyl protons in 14^\ominus could be determined straightforwardly from the positions of the ENDOR. signals (Fig. 2). Table 2 lists these coupling constants, along with the values $a_{H\mu}$ found for 14^\ominus when the solvent MTHF was replaced by DME. The tentative assignment of the coupling constants $a_{H\mu}$ to the eight ring protons in the positions $\mu = 1-4$ and $6-9$ (cf. Table 2 and

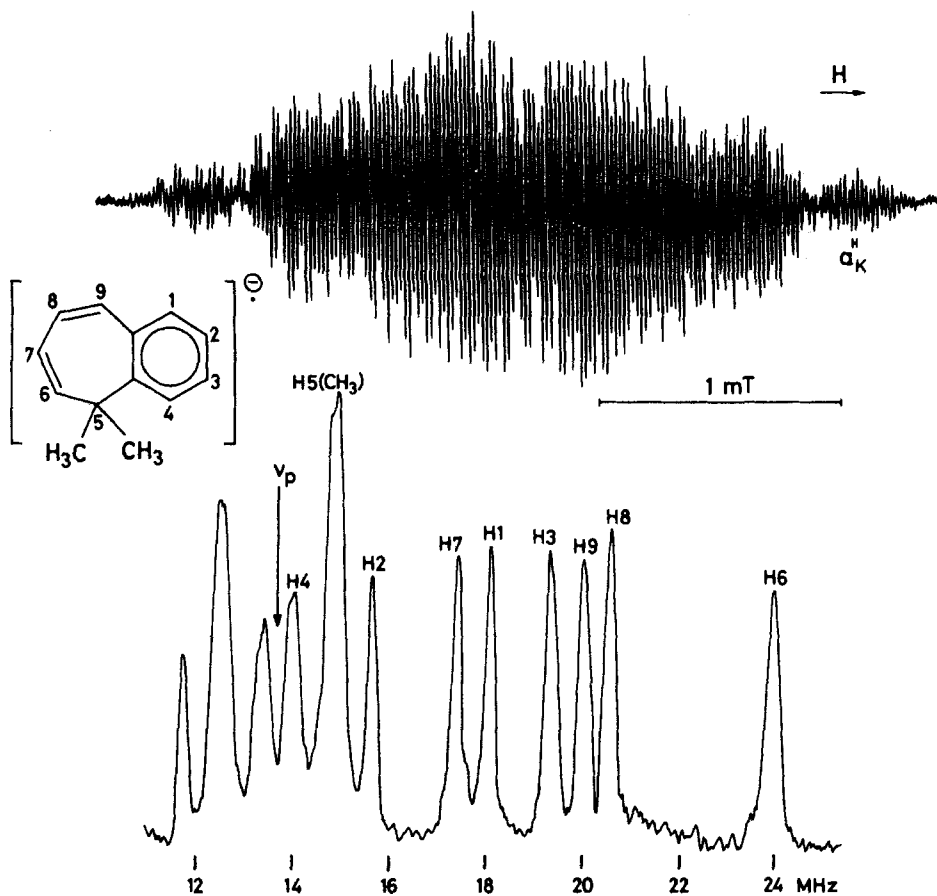


Fig. 2. ESR. and ENDOR. spectra of the radical anion of 5,5-dimethylbenzocycloheptene (**14**). Solvent: MTHF; counter-ion: K^\ominus ; temp.: 193 K. ν_p = frequency of the free proton.

Table 2. Coupling constants (in mT^a) for the radical anion of 5,5-dimethylbenzocycloheptene (**14**), the benzotropylium radical (**16**[•]) and the benzotropylium radical dianion (**16**[⊖])

Radical	14 [⊖]		16 [•]	16 [⊖] [16 -D ₄ [⊖]]
	MTHF/K [⊕]	DME/K [⊕]		
Solvent/ Counterion			high-boiling oil	
Temp. (K)	193	193	423	198
$\mu = 1$	0.316 (1H)	0.319 (1H)		
4	0.021 (1H)	0.010 (1H)	0.118 (2H)	0.006 (2H) [-0.001 (2D)]
2	0.140 (1H)	0.123 (1H)		
3	0.405 (1H)	0.341 (1H)	0.114 (2H)	0.271 (2H)
5	0.086 (6H ^b)	0.067 (6H ^b)		
9	0.455 (1H)	0.467 (1H)	0.816 (2H)	0.113 (2H) [0.113 (1H); 0.017 (1D)]
6	0.734 (1H)	0.739 (1H)		
8	0.493 (1H)	0.521 (1H)	0.292 (2H)	0.628 (2H) [0.628 (1H); 0.096 (1D)]
7	0.268	0.261 (1H)	1.103 (1H)	0.079 (1H)
<i>g</i> (± 0.0001)			2.0026	2.0027

^a) Experimental error ± 0.001 and ± 0.002 for coupling constants smaller and larger, respectively, than 0.1 mT.

^b) Protons of two methyl groups.

labelling of the ENDOR. signals in Fig. 2) is based on the correlation of the values $a_{H\mu}$ with the π -spin populations ρ_{μ} calculated by the *McLachlan* procedure [17] for the corresponding carbon centres μ in the radical anion of 1-phenyl-1,3-butadiene [18]. Like **12**[⊖] in MTHF, a hyperfine splitting, $a_K = 0.017$ mT, from the ³⁹K nucleus of the counter-ion was exhibited by the ESR. spectrum of **14**[⊖] in this solvent (Fig. 2).

1,6-Methano [10]annulene (1). As stated in the Introduction, previous studies of **1**[⊖] [1] attest to the high stability of this radical anion. In fact, temperatures above 323 K were required for an observation of a substantial decrease in the intensity of its ESR. spectrum. Experimental findings, which followed the disappearance of this spectrum, differed essentially for the two methods of preparation. When the decay of **1**[⊖] occurred during the electrolysis in DME (with Bu₄N[⊕]ClO₄[⊖] as the supporting salt), no ESR. signals of a secondary paramagnetic species were detected. On the other hand, when the radical anion **1**[⊖] was produced chemically with potassium in DME, and then allowed to decay, a novel paramagnetic species was subsequently generated by a renewed contact of the solution with the metallic mirror. The ESR. and ENDOR. spectra of this species, which has been identified as the benzotropylium radical dianion (**16**[⊖]), were also observed after the decay of the radical anions, **2**[⊖] to **5**[⊖], of the halogen-substituted derivatives of **1**. They will be dealt with in the next section.

11,11-Difluoro-1,6-methano [10]annulene (2). The ESR. spectra of the radical anions **2**[⊖] and **2**-D₄[⊖], generated electrolytically in DME at 213 K from **2** and its 2,5,7,10-tetradeuterio derivative, respectively, are shown in Figure 3 (Bu₄N[⊕]ClO₄[⊖] as the supporting salt). The analysis of these spectra yields readily the coupling

constants, $a_{H\mu}$, $a_{D\mu}$ and $a_{F\mu}$, of the protons, deuterons and ^{19}F nuclei. Their values are given in Table 3 which lists the known hyperfine data for the radical anions of 1,6-bridged[10]annulenes. The assignment of the value 0.082 mT to the two equivalent ^{19}F nuclei ($a_{F(11)}$) in 2^{\ominus} and 2-D_4^{\ominus} is unambiguous. The same holds for the remaining coupling constants, since, on passing from 2^{\ominus} to 2-D_4^{\ominus} , the value 0.554 mT ($a_{H(2,5,7,10)}$) is replaced by 0.085 mT ($a_{D(2,5,7,10)}$). Consequently, the coupling constant of 0.221 mT, due to the second set of four equivalent protons in 2^{\ominus} , is identified as $a_{H(3,4,8,9)}$.

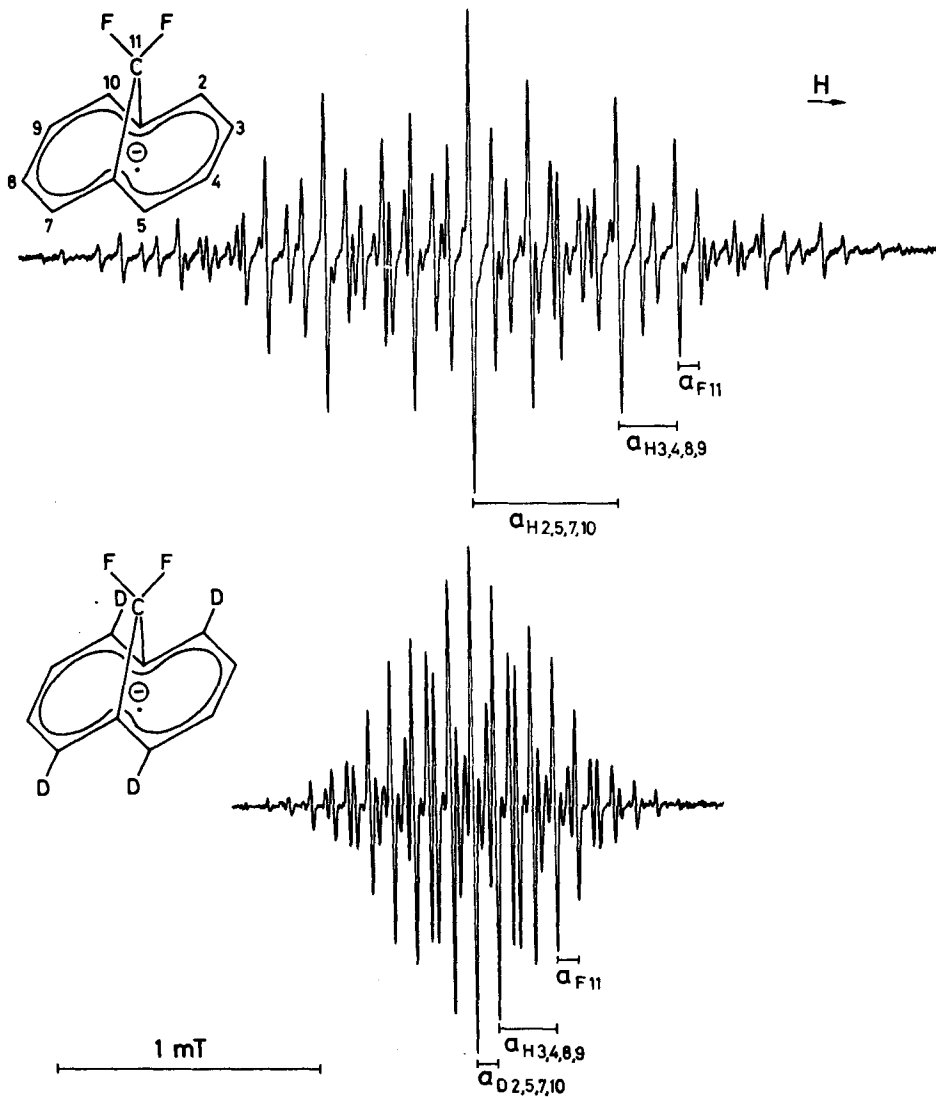


Fig. 3. ESR. spectra of the radical anions of 11,11-difluoro-1,6-methano[10]annulene (2) and its 2,5,7,10-tetradeuterio-derivative (2-D₄). Solvent: DME; counter-ion: Bu₄N[⊕]; temp.: 213 K.

Table 3. Coupling constants (in mT^a) for the radical anions of 1,6-*X*-bridged[10]annulenes **1** (*X*=CH₂)^b, **2** (*X*=CF₂), **3** (*X*=CHF), **7** (*X*=CHCOOH)^c, **8** (*X*=CO)^c, **9** (*X*=NH)^b, and **11** (*X*=O)^{b,c}

Radical anion	1 [⊖] [1-D ₄ ⊖]		2 [⊖] [2-D ₄ ⊖]	3 [⊖] [3-D ₄ ⊖]	
	DME/K [⊕]	DME/K [⊕]	DME/Bu ₄ N [⊕]	DME/Bu ₄ N [⊕]	
Solvent/ counterion					
Temp. (K)	183	293	213	213	
$\mu = 2,5; 7,10$	0.273 (4H)	0.240 (4H)	0.554 (4H)	0.079 (2H)	
	[0.043 (4D)]	[0.038 (4D)]	[0.085 (4D)]	0.076 (2H)	
3,4; 8,9	0.009 (4H)	0.023 (4H)	0.221 (4H)	[0.013 (4D)]	
				0.117 (2H)	
11	0.116 (2H)	0.106 (2H)	0.082 (2H)	0.084 (2H)	
				0.158 (1H, 1F)	
				0.089 (1H, 1F)	
$g (\pm 0.0001)$	2.0029	2.0028	2.0028	2.0030	

Radical anion	7 [⊖]	8 [⊖]	9 [⊖]	11 [⊖] [11-D ₄ ⊖]	
	DME/Bu ₄ N [⊕]	DMF/Et ₄ N [⊕]	DME/K [⊕]	DME/K [⊕]	DME/Bu ₄ N [⊕]
Solvent/ counterion					
Temp. (K)	223	213	193	193	193
$\mu = 2,5; 7,10$	0.222 (2H)	0.302 (4H)	0.328 (2H)	0.344 (4H)	0.358 (4H)
	0.205 (2H)		0.286 (2H)		
3,4; 8,9	0.029 (2H)	0.069 (4H)	0.028 (2H)	0.041 (4H)	0.034 (4H)
	0.019 (2H)		0.014 (2H)		
11	0.067 (1H)		0.058 (1N)		
			<0.005 (1H)		
$g (\pm 0.0001)$	2.0029	2.0028	2.0028	2.0027	2.0027

^a) Experimental error ± 0.001 and ± 0.002 mT for the coupling constants smaller and larger, respectively, than 0.1 mT.
^b) Ref. [1-3].
^c) Unpublished results.

The values $a_{H\mu}$, $a_{D\mu}$ and $a_{F\mu}$ for **2**[⊖] and **2-D₄**[⊖] were found to be almost independent of experimental conditions. They remained practically unaltered when chemical reduction of **2** and **2-D₄** with potassium in DME was used instead of electrolysis for the preparation of the radical anions. Moreover, the changes observed in these values upon variation of the temperature between 193 and 293 K did not exceed the limits of experimental error.

The radical anions **2**[⊖] and **2-D₄**[⊖], generated by either electrolytic or chemical method, were relatively stable at low temperature, but decayed appreciably above 293 K, as indicated by a gradual decrease in the intensities of their spectra. With the use of electrolysis, no new ESR. signals were observed after the disappearance of these spectra, unless traces of protic impurities were present in the solution. In such a case, raising slightly the voltage above that required for the genera-

tion of 2^{\ominus} and 2-D_4^{\ominus} [14] led to the appearance of the ESR. spectra due to the radical anions of 1,6-methano[10]annulene (**1**) and its 2,5,7,10-tetradeuterio-derivative (**1-D₄**), respectively [1] [3]. Again, different behaviour was found for the chemically produced radical anions. When, following the decay of 2^{\ominus} and 2-D_4^{\ominus} , the solutions were brought into a renewed contact with the potassium mirror, the ESR. and ENDOR. spectra, shown in *Figures 4* and *5*, appeared.

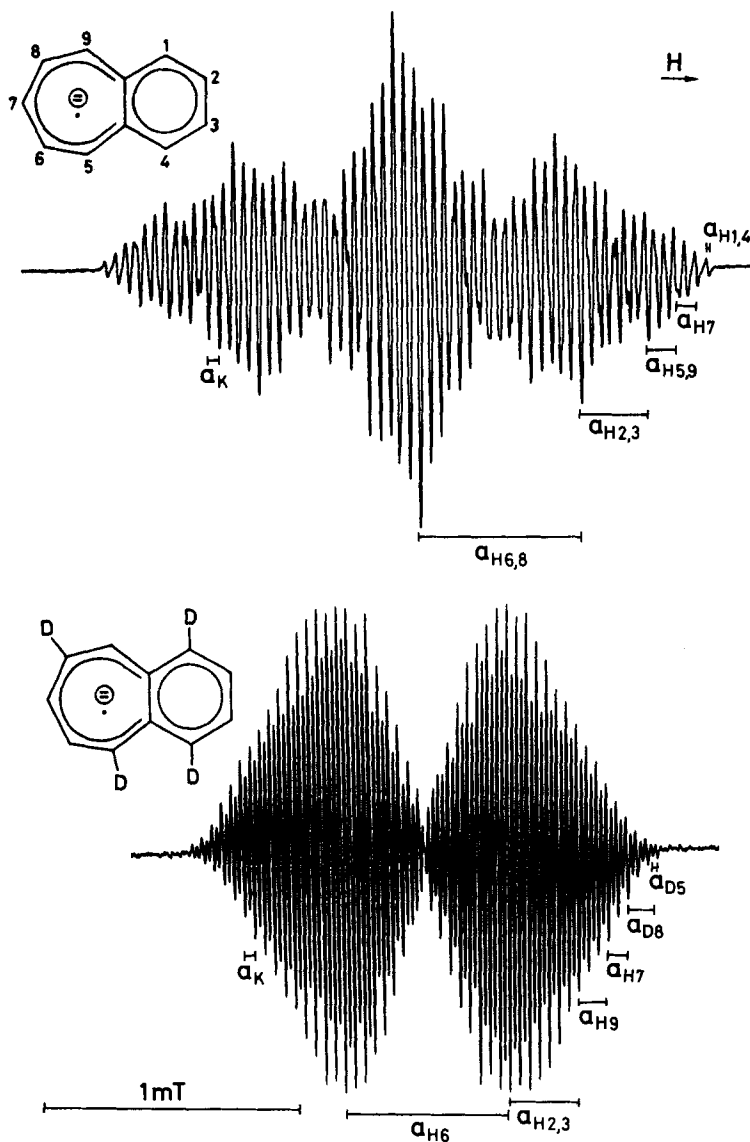


Fig. 4. ESR. spectra of the benzotropylium radical dianion (**16[⊖]**) and its 1,4,5,8-tetradeuterio-derivative (**16-D₄[⊖]**). Solvent: DME; counter-ion: K[⊖]; temp.: 198K.

The upper ones, stemming from **2** as the starting material, are those of the benzotropylium radical dianion (**16**[⊖]), since identical spectra were observed upon prolonged reaction of the cation **16**[⊕] with potassium in DME [18] [19]¹⁾. The pertinent coupling constants $a_{H\mu}$ are listed in *Table 2*. The two-proton values of 0.628 ($a_{H(6,8)}$), 0.271 ($a_{H(2,3)}$), 0.113 ($a_{H(5,9)}$) and 0.006 mT ($a_{H(1,4)}$) have been assigned by correlation with the π -spin populations ρ_μ calculated by the *McLachlan* procedure [17] for the carbon centres μ in **16**[⊖] [18]; the assignment of the one-proton value of 0.079 mT ($a_{H(7)}$) is obvious. The lower spectra in *Figures 4* and *5*, which were obtained from **2-D**₄ as the secondary product, must therefore arise from a deuterio-derivative of **16**[⊖]. The deuteriated positions are readily determined by comparison of the ENDOR. spectrum of **16**[⊖] with that of this derivative (*Fig. 5*). On passing from the former to the latter, the ENDOR. signal at 13.8 MHz (H(1,4)) disappears, while the intensities of the signals at 15.3 (H(5,9)) and 22.6 MHz (H(6,8)) are halved. This indicates that **2-D**₄[⊖] has been converted into 1,4,5,8-tetradeuteriobenzotropylium radical dianion (**16-D**₄[⊖]). It is confirmed by the analysis of the ESR. spectra (*Fig. 4*), in which the replacement of $a_{H(6,8)}$ (**16**[⊖]) by $a_{H(6)}$ and $a_{D(8)}$ (**16-D**₄[⊖]) transforms the three main groups of lines into two. This analysis, assisted by computer simulation, also reveals that a splitting, $a_K=0.035$ mT, from the ³⁹K nuclei of two equivalent counter-ions is present in the ESR. spectra of both **16**[⊖] and **16-D**₄[⊖].

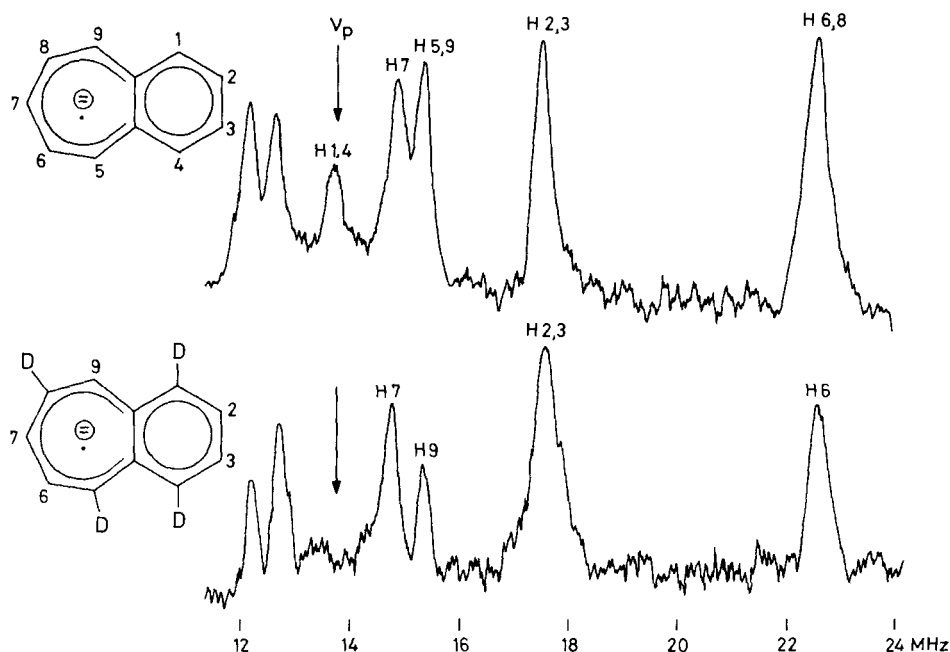
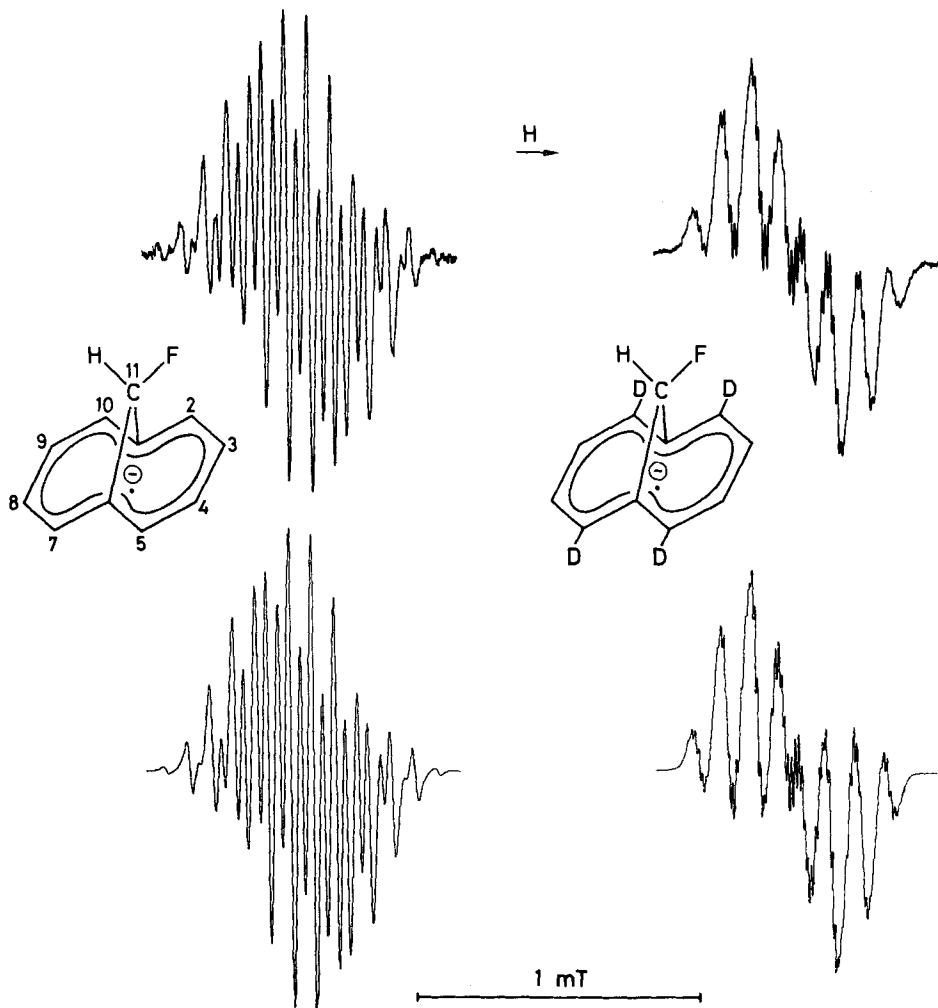


Fig. 5. ENDOR. spectra of the benzotropylium radical dianion (**16**[⊖]) and its 1,4,5,8-tetradeuterio-derivative (**16-D**₄[⊖]). Solvent: DME; counter-ion: K[⊕]; temp.: 198 K. ν_p = frequency of the free proton.

¹⁾ The ESR. spectrum of **16**[⊖] was first observed by *Bauld & Brown* [19a].

11-Fluoro-1,6-methano[10]annulene (3). The ESR. spectra of the radical anions 3^{\ominus} and 3-D_4^{\ominus} , shown in *Figure 6*, were taken under the same conditions (solvent: DME; counter-ion: $\text{Bu}_4\text{N}^{\oplus}$; temp.: 213 K) as those of 2^{\ominus} and 2-D_4^{\ominus} (*Fig. 3*). Also reproduced in *Figure 6* are the derivative curves which were simulated by computer with the use of the coupling constants $a_{\text{H}\mu}$, $a_{\text{D}\mu}$ and $a_{\text{F}\mu}$ given in *Table 3*. Since the symmetry of 3^{\ominus} (C_s) is lower than that of 2^{\ominus} (C_{2v}), deuteration in the positions $\mu=2,5,7,10$ led to a partial assignment only; it did not allow one to distinguish between $a_{\text{H}(2,5)}$ and $a_{\text{H}(7,10)}$ (0.079 and 0.076 mT) nor between $a_{\text{H}(3,4)}$ and $a_{\text{H}(8,9)}$ (0.117 and 0.084 mT). Furthermore, because the ENDOR. technique



*Fig. 6. ESR. spectra of the radical anions of 11-fluoro-1,6-methano[10]annulene (3) and its 2,5,7,10-tetradeuterio-derivative (3-D₄). Top: experimental spectra. Solvent: DME; counter-ion: $\text{Bu}_4\text{N}^{\oplus}$; temp.: 213 K. Bottom: spectra simulated with the use of the coupling constants given in *Table 3*; line-shape Lorentzian; line-width 0.01 mT.*

failed in this case (see Experimental Part), it was impossible to decide which of the two values observed for the nuclei at the bridging C-atom (0.158 and 0.089 mT) should be identified with $a_{H(11)}$ and which with $a_{F(11)}$.

For 3^{\ominus} and $3-D_4^{\ominus}$, as for 2^{\ominus} and $2-D_4^{\ominus}$, coupling constants $a_{H\mu}$, $a_{D\mu}$ and $a_{F\mu}$ did not depend on the nature of the counter-ion, and identical ESR. spectra were obtained at the same temperatures with either electrolytically or chemically produced radical anions in DME (counter-ions Bu_4N^{\oplus} and K^{\oplus} , respectively). However, in contrast to 2^{\ominus} and $2-D_4^{\ominus}$, the ESR. spectra of 3^{\ominus} and $3-D_4^{\ominus}$ exhibited a marked dependence on temperature, as evidenced by the striking changes in their total spreads. Thus, in the case of 3^{\ominus} , such a spread increased from 0.97 to 1.05 mT upon lowering the temperature from 223 (Fig. 6) to 193 K. The study of the changes in the individual coupling constants, responsible for this increase, was impaired by a poor spectral resolution below 213 K.

The radical anions 3^{\ominus} and $3-D_4^{\ominus}$ were substantially shorter-lived than 2^{\ominus} and $2-D_4^{\ominus}$ and decayed rapidly at temperatures as low as 243 K. Nevertheless, the secondary paramagnetic species observed after the disappearance of the original spectra (Fig. 6) were the same as in the case of **2** and $2-D_4$. Thus, electrolytic reduction in presence of protic impurities led, at a higher voltage, again to the radical anions 1^{\ominus} and $1-D_4^{\ominus}$, whereas the radical dianions 16^{\ominus} and $16-D_4^{\ominus}$ were the secondary products obtained chemically upon a renewed reaction of the solution with potassium.

11, 11-Dichloro-1, 6-methano [10]annulene (4) and 11-bromo-1, 6-methano [10]annulene (5). The life-times of the primary radical anions 4^{\ominus} and 5^{\ominus} were too short to permit their spectroscopic characterization, even at very low temperature (163 K; solvent: MTHF). The stability of the radical anions of the three halogen-substituted 1,6-methano[10]annulenes has thus been found to decrease in the order $2^{\ominus} > 3^{\ominus} > 4^{\ominus} \approx 5^{\ominus}$, i.e., with the introduction of two fluorine, one fluorine, two chlorine and one bromine atom into the bridging group.

Apart from the enhanced reactivity, the behaviour of **4** and **5** upon electrolytic and chemical reduction closely resembled that of **2** and **3**, since the secondary paramagnetic species were once more identical with those obtained for the latter radical anions.

The report on the radical anions of the four halogen-substituted 1,6-methano[10]annulenes, **2**, **3**, **4** and **5**, would not be complete without mentioning the preliminary results of the studies by polarography and cyclovoltametry [20]. The half-wave reduction potentials $E_{1/2}$ (values in V vs. Ag/AgCl/saturated KCl-electrode as reference; solvent: DMF; supporting salt: $Bu_4N^{\oplus}Br^{\ominus}$) are: **1**: -2.10; **2**: -1.89; **3**: -1.98; **4**: -2.08 and **5**: -2.08. It is noteworthy that in the polarograms of **4** and **5** additional waves are observed which are consistent with the loss of two chlorine anions and one bromine anion, respectively. The reversibility of the reduction to their primary radical anions was clearly established for **1** and its four halogen-derivatives **2-5**.

1,6-Methano [10]annulene-11-t-butyl-peroxyester (6). The ESR. spectrum of 6^{\ominus} could be obtained upon electrolytic reduction of **6** in DME at 198 K. Apart from the large line-width of 0.05 mT, it strongly resembled that of the radical anion of

1,6-methano[10]annulene-11-carboxylic acid (**7**) which is characterized by the hyperfine data in *Table 3*. A secondary paramagnetic species obtained electrolytically from 6^{\ominus} was identified as the radical anion of 1,6-oxido[10]annulene (**11**) [1], whereas reaction of **6** with potassium in DME at 193 K yielded directly a hitherto not observed ESR. spectrum²). Both methods afforded the radical anion of naphthalene as the final product. A fuller account of these results, which do not significantly pertain to the subject of the present paper, is given elsewhere [18]. More relevant to this subject were the investigations of the neutral peroxyester **6**.

Thermolysis of **6** in high-boiling oil at 363 K led to formation of a new diamagnetic material. This material turned strongly paramagnetic upon increasing the temperature to 423 K. The paramagnetic species has readily been recognized by its ESR. spectrum as the benzotropylium radical ($16\cdot$), since the product of one-electron reduction of the cation 16^{\oplus} gave rise to an identical spectrum under the same experimental conditions [18] [19]. The absence of paramagnetism at 363 K was found to be caused by conversion of the radical $16\cdot$ into a mixture of its dimers 16_2 . Only at higher temperatures (423 K), the equilibrium $16_2 \rightleftharpoons 2 16\cdot$ shifted sufficiently far to the right as to enable one to observe an intense ESR. spectrum of $16\cdot$. Such a spectrum is shown in *Figure 7*, and the coupling constants $a_{H\mu}$ determined therefrom are listed in *Table 2*. The assignment of the largest value of 1.103 mT, due to one proton, is straightforward ($a_{H(7)}$), while that of the four two-proton values of 0.816 ($a_{H(5,9)}$), 0.292 ($a_{H(6,8)}$), 0.118 ($a_{H(1,4)}$) and 0.114 ($a_{H(2,3)}$) is based on correlation with the π -spin populations ρ_{μ} calculated by the *McLachlan* procedure for the carbon centres μ in $16\cdot$ [18].

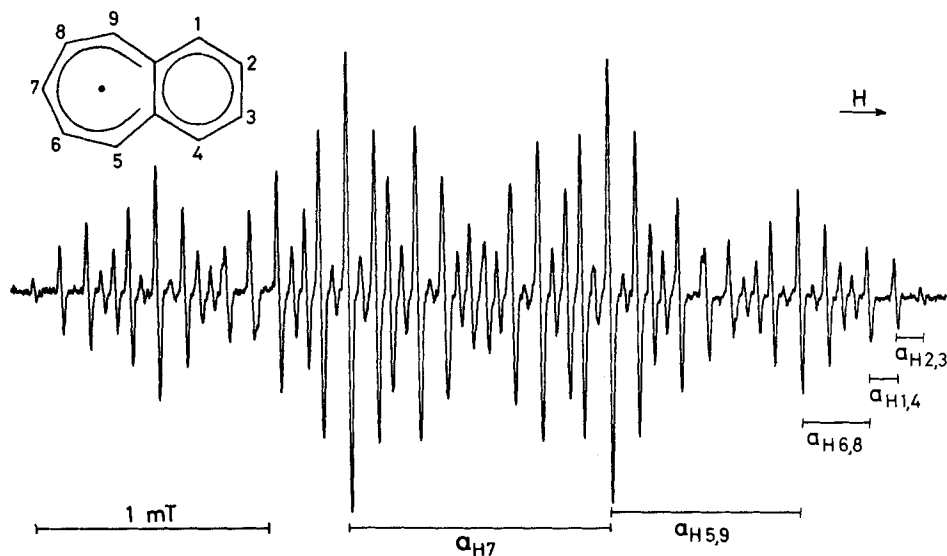


Fig. 7. ESR. spectrum of the benzotropylium radical ($16\cdot$). Solvent: high-boiling oil; temp.: 423 K.

²) The coupling constants derived from this spectrum, 0.17 (4 H), 0.08 (3 H) and 0.04 mT (2 H), suggest that it also arises from the radical anion of an 11-substituted 1,6-methano[10]annulene.

In contrast to the thermolysis of the peroxyester **6**, its photolysis (in hexane, at room temperature, by a high-pressure mercury lamp) yielded naphthalene as the main product.

Discussion. - *Spin distribution and structure.* According to their hyperfine data, the radical anions presented in *Tables 1* and *3* can be considered to belong to three classes denoted *A*, *B* and *C*.

Class A embraces the radical anions of 1,6-methano[10]annulene (**1**), 1,6-methano[10]annulene-11-carboxylic acid (**7**), 11-oxo-1,6-methano[10]annulene (**8**), 1,6-imino[10]annulene (**9**) and 1,6-oxido[10]annulene (**11**). The proton coupling constants $a_{H\mu}$, listed for these radical anions in *Table 3*, lie in the ranges $0.22 < a_{H(2,5)}, a_{H(7,10)} < 0.36$ and $0 < a_{H(3,4)}, a_{H(8,9)} < 0.07$ mT. They depend markedly on temperature, as demonstrated for **1**[⊖] in *Table 3*.

In previous detailed studies of **1**[⊖] [1] [3], it has been shown that the hyperfine data for **1**[⊖] are consistent with the assumption that this radical anion, like the neutral compound **1** [21], possesses the 'open' bicyclic structure of a 1,6-bridged[10]annulene. Both the unexpectedly low absolute values and the strong temperature dependence of the coupling constants $a_{H(2,5,7,10)}$ and $a_{H(3,4,8,9)}$ can be rationalized in terms of non-planarity of the ten-membered π -perimeter. This interpretation is fully supported by the hyperfine data for the radical anion of 2-methyl-1,6-methano[10]annulene [22]. It is noteworthy that, despite their pronounced effect on the coupling constants $a_{H\mu}$, the deviations of the π -system from planarity do not seriously impair the cyclic electron delocalization in **1**[⊖]. Apparently, the angles between the $2p_z$ -AO's of the linked carbon centers in the perimeter should not be identified with the relatively large twist angles determined by X-ray crystallographic structure analysis of 1,6-methano[10]annulene-2-carboxylic acid [23]. Rather, the deviations of such $2p_z$ -axes from parallel arrangement must be distributed over the cyclic π -system in such a way that the losses in the delocalization energy are minimized [24].

The comparable values and similar temperature dependence of the pertinent coupling constants $a_{H\mu}$ indicate that the radical anions **7**[⊖], **8**[⊖], **9**[⊖] and **11**[⊖] also retain the 'open' [10]annulene structure of the corresponding neutral compounds [11] [25]. This statement must hold for **8**[⊖], **9**[⊖] and **11**[⊖] even more than for **1**[⊖], since the replacement of the CH_2 -bridging group by CO, NH and O, respectively, is expected to lead to a larger distance between the bridged C-atoms C(1) and C(6).

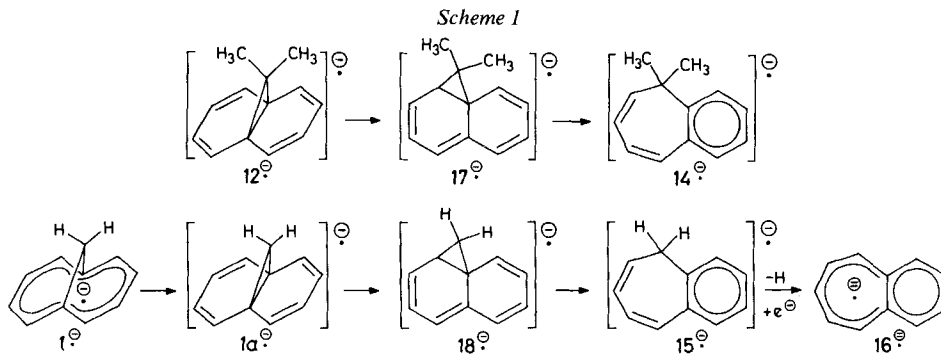
In addition to the above mentioned radical anions, those of 1,6-methano[10]annulene-11-*t*-butyl-peroxyester (**6**) (see Results) and 1,6-methylimino[10]annulene (**10**) [2] should also be considered as belonging to *Class A*. Although their ESR spectra have not been analyzed in full detail, their hyperfine patterns point to a close structural relationship with **7**[⊖] and **9**[⊖], respectively.

Class B consists of the radical anions of 11,11-dimethyl-tricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene (**12**) and *cis*-9,10-(2-oxa-propano)-9,10-dihydronaphthalene (**13**). The coupling constants $a_{H(2,5,7,10)}$ and $a_{H(3,4,8,9)}$ given in *Table 1* for **12**[⊖] (0.416 and 0.175 mT) and **13**[⊖] (0.380 and 0.151 mT) exceed markedly those found for the radical anions of *Class A*. Moreover, in contrast to the latter, they depend only slightly on temperature. It is essential to note that these coupling constants

approximately match the halves of the values, $a_{H(1,4)}=0.762$ and $a_{H(2,3)}=0.279$ mT, reported for the radical anion of *trans*-1,3-butadiene [16]. Such a relationship indicates that each of the radical anions **12**[⊖] and **13**[⊖] contains twice the butadiene π -system. In other words, the tricyclic 'bisnorcaradiene' structure must be preserved on passing from the neutral compounds **12** [12] and **13** [26] to their radical anions. As shown by an X-ray crystallographic structure analysis of **12** [27], the C(1),C(6) interatomic distance is 182 pm, as compared with 226 pm found for 1,6-methano[10]annulene-2-carboxylic acid [23]. The two butadiene π -system in **12** are almost planar and their planes form an angle of *ca.* 130°.

Class C comprises the radical anions of 11,11-difluoro-1,6-methano[10]annulene (**2**) and 11-fluoro-1,6-methano[10]annulene (**3**). Apart from the fluoro-substitution, the common feature of **2**[⊖] and **3**[⊖] is that their coupling constants $a_{H\mu}$ ($\mu=2$ to 10), listed in *Table 3*, do not resemble the corresponding data for the radical anions of either *Class A* (*Table 3*) or *B* (*Table 1*). Whereas **2**[⊖] surprises one by the large values of both $a_{H(2,5,7,10)}$ (0.554 mT) and $a_{H(3,4,8,9)}$ (0.221 mT), the peculiarity of **3**[⊖] is the low values of $a_{H(2,5)}$ and $a_{H(7,10)}$ (0.079; 0.075 mT). Furthermore, while the coupling constants for **2**[⊖] are almost insensitive to variations in temperature, the ESR. spectrum of **3**[⊖] displays a remarkably large temperature dependence (reduction in the total spectral spread by 0.08 mT on going from 193 to 223 K *vs.* a corresponding decrease of only 0.02 mT for **1**[⊖] in the same range [3]).

The interpretation of all these experimental findings meets with great difficulties. An X-ray crystallographic structure analysis of the difluoro-derivative **2** [28] reveals only slight differences in the geometry of the ten-membered perimeter with respect to the 2-carboxylic acid of the parent hydrocarbon **1** [23]. Particularly, the C(1),C(6)-distances in both molecules are non-bonding and equal within the limits of experimental error (226 ± 1 pm). The compound **2** thus has the 'open' structure of 1,6-bridged[10]annulenes and, according to the ¹H-NMR. spectra [8], the same should hold for the monofluoro-derivative **3**. The hyperfine data for **2**[⊖], **2-D₄**[⊖], **3**[⊖] and **3-D₄**[⊖] give evidence that on passing from the respective neutral compounds to their radical anions neither the symmetries nor the numbers of interacting nuclei have changed. Moreover, the cyclovoltametry of **2** and **3** [20] indicates that no drastic changes in geometry are probable on such a passage. Thus, the unusual values of the coupling constants for **2**[⊖] and **3**[⊖] must involve

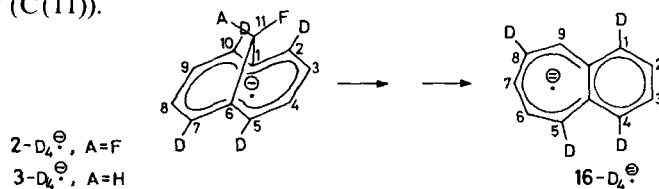


some substantial alterations in the character of the singly occupied orbital, as a consequence of the substitution by fluorine ('fluoro-effect'). In order to provide a theoretical rationale for these changes, more information is required. In particular, the signs of the coupling constants are of paramount importance in this respect.

Formation of benzocycloheptene and benzotropylium derivatives. In a previous communication [4], we have briefly discussed the valence isomerization of the radical anion of 11,11-dimethyltricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene (**12**) to that of 5,5-dimethylbenzocycloheptene (**14**). This isomerization, which takes place already at 163 K (see Results), was found to require *ca.* 100 kJ mol⁻¹ less activation energy than the corresponding conversion, **12** to **14**, occurring with the neutral compound above 423 K [4] [6]. In analogy to the rearrangement described by *Berson & Willcott* [29] for a norcaradiene/cycloheptatriene-system, the reaction **12**[⊖] to **14**[⊖] should proceed *via* the transient isomer **17**[⊖], as illustrated by *Scheme 1*. Also described by this Scheme is the course of reaction proposed for the conversion of the radical anion of 1,6-methano[10]annulene (**1**) to benzotropylium radical dianion (**16**[⊖]). It is assumed that such a conversion involves an intermediate occurrence of the radical anions **1a**[⊖], **18**[⊖] and **15**[⊖] which are analogous to **12**[⊖], **17**[⊖] and **14**[⊖], respectively.

The failure to observe the radical anion of 5*H*-benzocycloheptene (**15**) is due to the fact that under the experimental conditions employed (contact with potassium) **15**[⊖] is rapidly converted into **16**[⊖] [18] [19]. It is important to note that the isomerization of the neutral compound **1** to **15** can also be realized, albeit above 673 K [13]. It is therefore tempting to suggest that the considerably higher temperatures required for the *Berson-Willcott*-type rearrangements [29] of **1** and **1**[⊖] relative to **12** and **12**[⊖], respectively, reflect the different structures of the former and latter species. Whereas the cross-link of the benzocycloheptene system is preformed in **12** and **12**[⊖], a C(1),C(6)-bonding interaction has to develop in **1** and **1**[⊖]. This means that the valence isomerization of **1** and **1**[⊖] into the tricyclo[4.4.1.0^{1,6}]undeca-2,7,4,9-tetraene (**1a**) and its radical anion (**1a**[⊖]), respectively, is expected to constitute the first and rate determining step of the reactions in question.

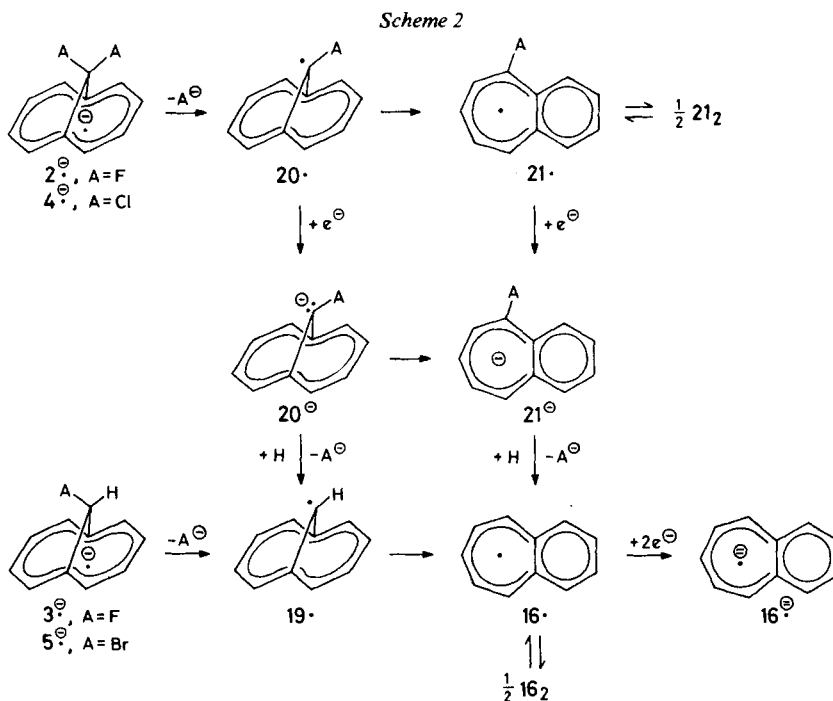
At first sight, it seems that the same *Scheme 1* might also apply to the radical anions of 11,11-difluoro- (**2**), 11-fluoro- (**3**), 11,11-dichloro- (**4**) and 11-bromo-1,6-methano[10]annulene (**5**), since the chemical reduction of these halogen-substituted derivatives of **1** also yields the benzotropylium radical dianion (**16**[⊖]) as the final paramagnetic product (see Results). Moreover, the conversion of the 2,5,7,10-tetradeuteriated radical anions **2-D₄**[⊖] and **3-D₄**[⊖] into the 1,4,5,8-tetradeuterio-benzotropylium radical dianion (**16-D₄**[⊖]) is compatible with *Scheme 1*, because it bears out the expectation that the C-atom 9 in **16**[⊖] stems from the bridging group of **2**[⊖] and **3**[⊖] (C(11)).



However, other findings point out that a different reaction scheme should be valid for the rearrangements of 2^{\ominus} - 5^{\ominus} into 16^{\ominus} , and of 2-D_4^{\ominus} or 3-D_4^{\ominus} into 16-D_4^{\ominus} . The arguments in support of this statement are advanced below.

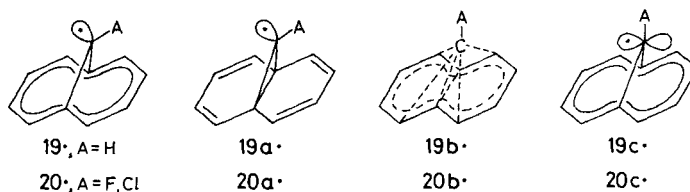
First of all, according to previous studies of 2,5-semiquinones derived from **1** and **2** [30], one expects that the tendency to form the C(1),C(6)-bond will decrease in the order $1^{\ominus} > 3^{\ominus} > 2^{\ominus}$, as a consequence of the fluoro-substitution. Since the formation of such a bond is the rate determining step in *Scheme 1*, the reactivity of the three radical anions should diminish in the same order. In fact, an opposite sequence has been found experimentally, as the minimum temperatures required for the conversion of 1^{\ominus} , 3^{\ominus} and 2^{\ominus} to 16^{\ominus} are 323, 293 and 243 K, respectively.

A further argument, which pleads against the *Scheme 1* for 2^{\ominus} , 3^{\ominus} , 4^{\ominus} and 5^{\ominus} is the behaviour of the corresponding neutral compounds upon thermolysis. Unlike **12** and **1**, these halogen-substituted compounds do not undergo a *Berson-Willcott*-type rearrangement, but yield naphthalene as the major product at high temperatures [5-11]. Obviously, in contrast to **12** and **1**, the uptake of an additional electron by **2**, **3**, **4** and **5** to form the respective radical anions, not only enormously enhances the reactivity, but also changes the course of reaction. The loss of a halogen anion by 2^{\ominus} , 3^{\ominus} , 4^{\ominus} and 5^{\ominus} suggests itself as the first and rate determining step in the conversion of these radical anions to 16^{\ominus} . The occurrence of such a step is evidenced by polarographic reduction of **4** and **5** where additional waves are consistent with a rapid elimination of two chlorine anions by 4^{\ominus} and of



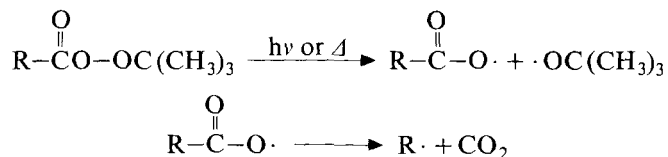
one bromine anion by 5^\ominus . (An analogous loss of two and one fluorine anions by 2^\ominus and 3^\ominus , respectively, is evidently too slow to be observed in the polarograms of **2** and **3**.) The finding that 4^\ominus and 5^\ominus react much more easily than 2^\ominus and 3^\ominus is readily accounted for, since Cl^\ominus and Br^\ominus are substantially better leaving groups than F^\ominus .

Scheme 2 presents the course of reaction proposed for the conversion of the four halogen-substituted radical anions to 16^\ominus . The essential part of such a scheme, which also accounts for the conversion of 2-D_4^\ominus and 3-D_4^\ominus into 16-D_4^\ominus (see above), is the transient existence of the radicals **19** \cdot and **20** \cdot . Since under the conditions where these radicals were formed in the present work they are too short-lived to be characterized by ESR. spectroscopy, no information about their structure is yet available. Further experiments are, however, planned, which may make up for this deficiency. Presumably, as formulated in *Scheme 2*, the singly occupied orbital has rather σ -(**19** \cdot , **20** \cdot) than π -character (**19c** \cdot , **20c** \cdot), i.e., the radical centre C(11) is pyramidal and not planar, like those in structurally related species [31]. Alternative structures, which would favour the rearrangement of **19** \cdot and **20** \cdot into **16** \cdot and **21** \cdot , respectively, should also be considered. Such structures involve either cyclopropyl type σ -radicals (**19a** \cdot , **20a** \cdot) [32], or 'non-classical' species (**19b** \cdot , **20b** \cdot), similar to that proposed for the $[\text{C}(\text{CH}_3)]_6$ -dication [33].

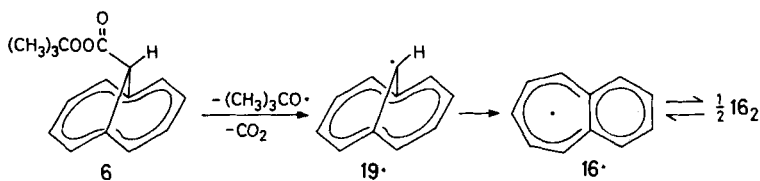


The occurrence of the transient radical **19** \cdot is also indicated by the electrolytic reduction of **2**, **3**, **4** and **5** which, in presence of traces of protic impurities, leads to the radical anion of 1,6-methano[10]annulene (**1**) as the final product (see Results). Under these conditions, a formal addition of a H-atom to **19** \cdot must be more rapid than the rearrangement of **19** \cdot to benzotropylium radical (**16** \cdot). The resulting 1,6-methano[10]annulene (**1**) can be transformed by further electrolysis into its radical anion (1^\ominus), whereby, in the case of the fluoro-derivatives, the required increase in the voltage corresponds to the more negative polarographic half-wave reduction potentials of **1** vs. **2** and **3** (differences of -0.21 and -0.12 V, respectively).

The most convincing evidence in favour of the transient existence of **19** \cdot is provided by the thermolysis of 1,6-methano[10]annulene-11-*t*-butylperoxyester (**6**). The *t*-butyl-peroxyesters are known to undergo easily a cleavage of the O-O-bond on photolysis [31] [34] or thermolysis [35]. The resulting loss of a *t*-butoxy group is, in general, immediately followed by decarboxylation.



In the case of the *t*-butyl-peroxyester **6**, the radical $R\cdot$ is the transient species **19** \cdot , the occurrence of which should be signaled by the observation of its rearrangement product, the valence isomer **16** \cdot . In fact, the benzotropylium radical (**16** \cdot) can be directly identified as the final product of the thermolysis of **6** in high-



boiling oil (see Results), since under these conditions the high temperature required for a substantial dissociation of the dimers **16**₂ (423 K) [18] [19] is readily achieved. In contrast, such a temperature is inaccessible for reactions in DME-solution, so that the ESR. evidence for the rearrangement of **19** \cdot into **16** \cdot is only obtained indirectly by the observation of the benzotropylium radical dianion (**16**²⁻) (Scheme 2).

The finding that photolysis of *t*-butylperoxyester **6** fails to produce **16** \cdot via **19** \cdot is accounted for by the presence of the cyclic π -system which has a strong absorption in the region of radiation (254 nm). This feature distinguishes **6** from the previously studied compounds $R(\text{CO})\text{OOC}(\text{CH}_3)_3$ when $R\cdot$ is an alkyl fragment. It is assumed that the excitation of the ten-membered π -perimeter is transferred to the adjacent C(1),C(11)- and C(6),C(11)-bonds rather than to the O,O-linkage of the peroxyester group. The cleavage of these bonds leads to formation of naphthalene, as actually observed (see Results). Examples for analogous, photochemically induced cleavages of single bonds, which are adjacent to π -systems, have been amply reported [36].

Conclusions. - The 1,6-bridged[10]annulenes and their radical anions not only represent model compounds for a perturbed ten-membered perimeter, but also provide suitable starting material for the study of chemical reactions. Two distinct types of such reactions are found to occur: (1) loss of the bridging group to yield naphthalene (or, in some cases, the isomeric azulene) and (2) the rearrangement to benzocycloheptene and benzotropylium π -system. For both types of reactions, the rates are enormously increased on passing from the neutral compounds to their radical anions. This point is illustrated by the present paper which deals primarily with the reactions of the second type. Such reactions are of considerable chemical interest, since they can be regarded as analogous to the *Berson-Willcott* rearrangement observed for a norcaradiene-cycloheptatriene system. It is hoped that the examples described in this paper will give some insight into the mechanism of such a rearrangement.

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