

283. The Radicals and Radical Dianions of Bridged [11]- and [15]Annulenyls as Compared with Those of Benzotropylyl and 2,3-Naphthotropylyl

by Fabian Gerson and Walter Huber

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

and Klaus Müllen

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

Herrn Professor Dr. *Edgar Heilbronner* zu seinem 60. Geburtstag gewidmet

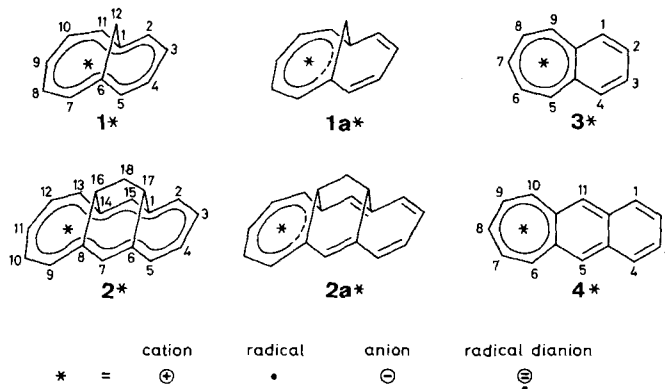
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Summary

The 1,6-methano[11]annulenyl ($\mathbf{1}\cdot$), 1,6:8,14-propane-1,3-diylidene[15]annulenyl ($\mathbf{2}\cdot$), benzotropylyl ($\mathbf{3}\cdot$) and 2,3-naphthotropylyl ($\mathbf{4}\cdot$) radicals have been characterized by their ESR. spectra. The corresponding radical dianions, $\mathbf{1}^{\ominus}$, $\mathbf{2}^{\ominus}$, $\mathbf{3}^{\ominus}$ and $\mathbf{4}^{\ominus}$, have also been studied both by ESR. and ENDOR. spectroscopy. Assignment of the coupling constants $a_{\text{H}\mu}$ to protons in the individual positions μ of these radicals and radical dianions is to a large extent based on investigations of specifically deuteriated derivatives. The radicals $\mathbf{1}\cdot$, $\mathbf{2}\cdot$, $\mathbf{3}\cdot$ and $\mathbf{4}\cdot$ exist in temperature-dependent equilibria with $(\mathbf{1})_2$, $(\mathbf{2})_2$, $(\mathbf{3})_2$ and $(\mathbf{4})_2$, respectively, where $(\mathbf{1})_2$ to $(\mathbf{4})_2$ denote mixtures of dimers of $\mathbf{1}\cdot$ to $\mathbf{4}\cdot$. The dissociation enthalpies, ΔH° , of $(\mathbf{1})_2$ (102 kJ/mol) and $(\mathbf{2})_2$ (88 kJ/mol) are considerably smaller than those of $(\mathbf{3})_2$ and $(\mathbf{4})_2$ which do not significantly differ from the ΔH° value of bitropylyl (139 ± 6 kJ/mol). This finding indicates that the gain in π -electron delocalization energies, $\Delta(DE)_\pi$, upon dissociation markedly increases on going from bitropylyl, $(\mathbf{3})_2$ and $(\mathbf{4})_2$ to $(\mathbf{1})_2$ and $(\mathbf{2})_2$, and thus points to an additional 'resonance stabilization' of $\mathbf{1}\cdot$ and $\mathbf{2}\cdot$, as compared with $\mathbf{3}\cdot$ and $\mathbf{4}\cdot$. A more pronounced π -spin localization on the 7-membered ring is observed in $\mathbf{3}\cdot$, $\mathbf{4}\cdot$, $\mathbf{3}^{\ominus}$ and $\mathbf{4}^{\ominus}$ relative to the corresponding species, $\mathbf{1}\cdot$, $\mathbf{2}\cdot$, $\mathbf{1}^{\ominus}$ and $\mathbf{2}^{\ominus}$. It can be interpreted in terms of simple π -perimeter models without explicitly invoking substantial homoconjugative interactions between the bridged centres in $\mathbf{1}\cdot$, $\mathbf{2}\cdot$, $\mathbf{1}^{\ominus}$ and $\mathbf{2}^{\ominus}$. However, the shortcomings of these crude models do not allow one to make a clear-cut statement about the contributions of the homotropylyl structures to the π -systems of these paramagnetic species. The radical dianions $\mathbf{1}^{\ominus}$ and $\mathbf{2}^{\ominus}$ exhibit considerable hyperfine splittings from one ^{23}Na or ^{39}K nucleus of the counter-ion, whereas for $\mathbf{3}^{\ominus}$ and $\mathbf{4}^{\ominus}$ such splittings stem from two equivalent alkali metal nuclei. This finding is readily rationalized by different geometries of the bridged annulenyls and their benzo- and naphthotropylyl analogues. Hyperfine data are also given for the radical anions

of 7*H*-benzocycloheptene, (**3-H**)[⊖], and 6*H*-(2,3-naphtho)cycloheptene, (**4-H**)[⊖], as well as for the radical dianion of 1,6:8,14-bismethano[15]annulenyli, **5**[⊖].

Introduction. - The 1,6-methano[11]annulenylium (**1**[⊕]) [1] and 1,6:8,14-propane-1,3-diylidene[15]annulenylium (**2**[⊕]) [2] ions are considered as higher homologues of the 'aromatic' tropylium ion. It is a matter of controversy to what extent the respective homotropylium structures, **1a**[⊕] and **2a**[⊕] contribute to the π -systems of **1**[⊕] and **2**[⊕], and such a contribution has, in particular, been discussed for the cation **1**[⊕] which was studied by several experimental and theoretical methods [3].



In the present paper the ESR. spectra of the radicals **1**[•] and **2**[•] are described, along with those of the radical dianions **1**^{⊖⊖} and **2**^{⊖⊖} which could also be investigated by the ENDOR. technique. It was hoped that the contributions of the corresponding homotropyli structures (**1a**[•], **2a**[•], **1a**[⊖] and **2a**[⊖]) to the π -systems of **1**[•], **2**[•], **1**[⊖] and **2**[⊖] might be deduced by comparing the proton hyperfine data for these radicals and radical dianions with the values measured for their benzotropyli- and 2,3-naphthotropyli analogues (**3**[•], **4**[•], **3**[⊖] and **4**[⊖]).

For the sake of assignment of coupling constants to the protons in the individual positions, several specifically deuteriated derivatives have also been studied in the two series.

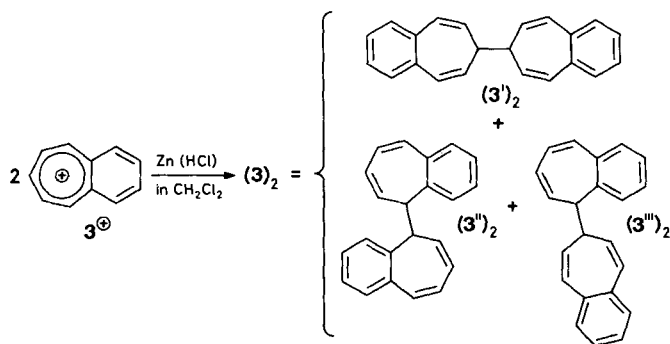
Finally, in order to assess the relative π -delocalization energies of **1**[•], **2**[•], **3**[•] and **4**[•], the dissociation enthalpies of their dimers (**1**)₂, (**2**)₂, (**3**)₂ and (**4**)₂ have been determined.

The benzotropyli radical (**3**[•]) was postulated as an intermediate in several reactions [4] [5]. Its ESR. spectrum was first observed in our Basle laboratory upon thermolysis of 1,6-methano[10]-annulene-11-*t*-butylpercarboxylate [5] [6]. The corresponding radical dianion (**3**^{⊖⊖}) was obtained some time ago by *Bauld & Brown* [7] through reaction of 5-benzotropyliumethylether with Na in THF, but the analysis of the ESR. spectrum made by these authors is partly incorrect. Later, the ESR.- and ENDOR. spectra of **3**^{⊖⊖} were observed in the course of our studies on paramagnetic species produced by reduction of 1,6-methano[10]annulene and its 11-halogenated derivatives with potassium in 1,2-dimethoxyethane [5] [6]. An analogous treatment of [2,5,7,10-²H₄]-11,11-difluoro-1,6-methano[10]-annulene led to the ESR.- and ENDOR. spectra attributed to the [1,4,5,8-²H₄]benzotropyli radical dianion [5] [6]. The 2,3-naphthotropyli radical was proposed as an intermediate in the thermal

decomposition of derivatives of 2,3-(2',3'-naphtho)norcaradiene [4b], but its ESR. spectrum was not reported. Thus except for 3^\oplus and 3^\ominus , which were characterized in our preceding paper [5], the only reference to the ESR.- and ENDOR. spectra of the paramagnetic species dealt with in the present work is a Ph.D. thesis of one of us [6].

Experimental Part. - *Source of compounds.* The BF_4^\ominus salts of the 1,6-methano[11]annulenylium (1^\oplus) and 1,6:8,14-propane-1,3-diylidene[15]annulenylium (2^\oplus) ions were kindly provided by Prof. E. Vogel. Their deuterio-derivatives were prepared analogously to the parent cations [1] [2], i.e., with the use of deuteriated dialdehydes or Wittig reagents. A description of these syntheses is given in [6]. The same methodology was applied to the preparation of the BF_4^\ominus salts of the benzotropylium (3^\oplus) and 2,3-naphthotropylium (4^\oplus) ions. Each of the four cations, 1^\oplus to 4^\oplus , was converted into a mixture of dimers of the respective radical, 1^\cdot to 4^\cdot . The procedure leading to such mixtures, henceforth denoted as $(1)_2$ to $(4)_2$, is described in the following for the reaction $2 \times 3^\oplus + 2e^\ominus \rightarrow (3)_2$ as an example¹⁾.

50 mg of $3^\oplus \text{BF}_4^\ominus$ in 20 ml CH_2Cl_2 were treated with 0.5 g Zn dust and a drop of conc. HCl. The suspension was stirred for 15 min until the yellow colour of 3^\oplus disappeared. Removal of the metal, evaporation of the solvent, and chromatography on silica gel yielded 30 mg of white amorphous material which was identified as $(3)_2$ by MS. (parent peak 282). According to its ^{13}C -NMR. spectrum, $(3)_2$ consisted of three isomeric dimers, of which the one with the highest symmetry, $(3')_2$, represented the major component (ca. 80%), while the two others, $(3'')_2$ and $(3''')_2$, were present in much smaller amounts (ca. 10% each).



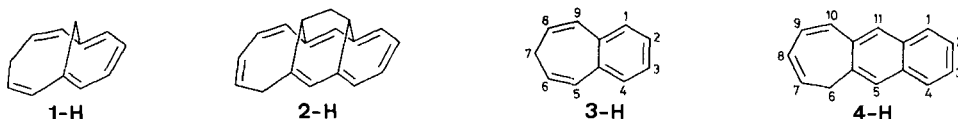
Recrystallization from CHCl_3 gave the pure dimer $(3')_2$; white needles, m.p. 108° ; ^{13}C -NMR. (CDCl_3 ; ppm relative to TMS) 136.8, 132.1, 130.2, 129.7, 126.1, 40.2.

Although the corresponding products, $(1)_2$, $(2)_2$ and $(4)_2$, of 1^\oplus , 2^\oplus and 4^\oplus , respectively, were not analyzed as thoroughly as $(3)_2$, it can reasonably be assumed that they also consisted of three isomeric dimers analogous to $(3')_2$, $(3'')_2$ and $(3''')_2$, and that the symmetric $(3')_2$ -like components predominated in the mixtures.

Preparation of the paramagnetic species. The neutral radicals, 1^\cdot to 4^\cdot , were obtained by homolytic cleavage of $(1)_2$ to $(4)_2$, respectively, in high-boiling oil at temperatures ranging from 80 to 160° . Because of the equilibria, $2 \times 1^\cdot \rightleftharpoons (1)_2$ to $2 \times 4^\cdot \rightleftharpoons (4)_2$ (see Results), the ESR. studies had also to be performed at these elevated temperatures. Despite the relative persistence of the radicals, no use could be made of the ENDOR. technique under such conditions.

The radical dianions, 1^\ominus to 4^\ominus , were prepared from three types of starting material by reaction with an alkali metal (K or Na) in 1,2-dimethoxyethane (DME) or THF. The three types of material were the cations, 1^\oplus to 4^\oplus , the dimer mixtures, $(1)_2$ to $(4)_2$, and their hydrocarbon precursors, 1-H to 4-H.

¹⁾ The reaction of $3^\oplus \text{BF}_4^\ominus$ with Zn was also carried out by other authors [4a], but, contrary to our results, failed to produce the expected dimer mixture $(3)_2$.



The ESR. spectra of 1^{\ominus} to 4^{\ominus} were taken in the temperature range between -90 and 0° . The apparatus comprised a *Varian-ENDOR.-1700-system* attached to a *Varian-ESR.-E9* spectrometer. For the coupling constants of the protons $a_{H\mu} > 0.1$ mT and for those of ^{23}Na and ^{39}K nuclei, the experimental error amounted to ± 0.002 mT; in the case of $a_{H\mu} < 0.1$ mT it was estimated as ± 0.001 mT.

As evidenced by ESR.- and ENDOR. characterization of $(3\text{-H})^{\ominus}$ and $(4\text{-H})^{\ominus}$ (see *Appendix 1*), the first step in the reaction of the hydrocarbons, **1-H** to **4-H**, with an alkali metal in DME or THF must be the formation of the respective radical anions. The second step is presumably the loss of a hydride anion to yield the neutral radicals, **1·** to **4·**, in equilibria with the mixtures of their dimers.

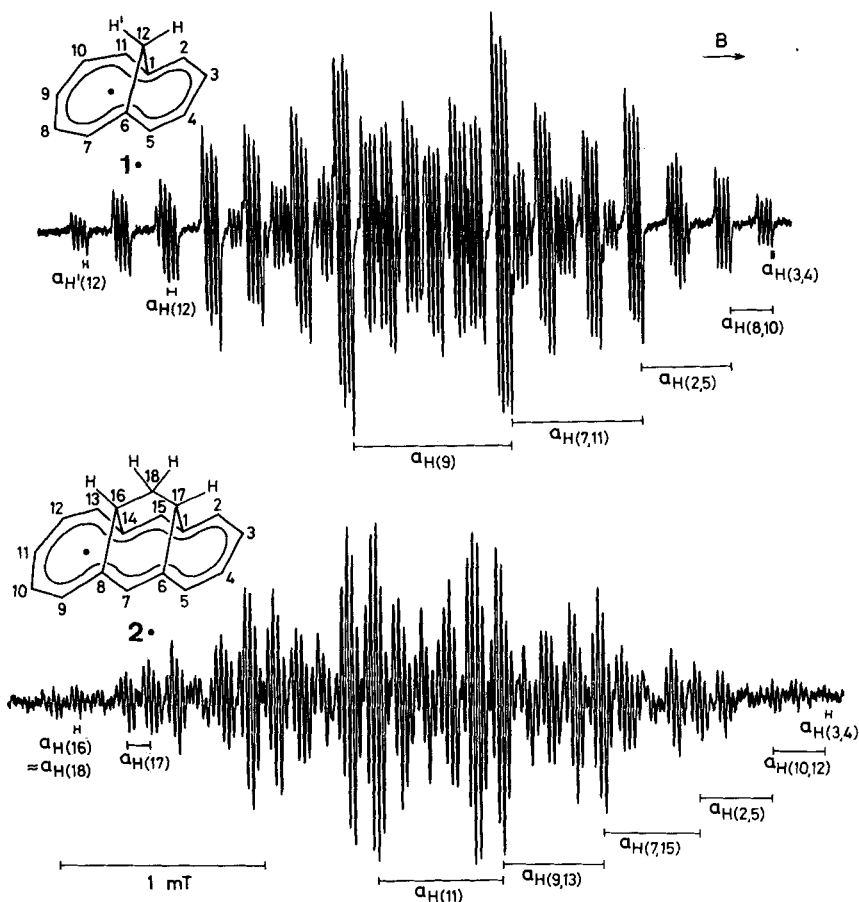
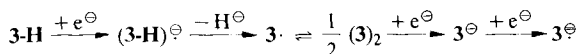


Fig. 1. ESR. spectra of the 1,6-methano[11]annulenyl (**1·**) and 1,6:8,14-propane-1,3-diylidene[15]annulenyl (**2·**) radicals (Solvent: high-boiling oil; temperature: 383 (**1·**) and 353 K (**2·**))

(1)₂ to (4)₂. These are subsequently reduced to the radical dianions, 1[⊖] to 4[⊖], with the intermediacy of the diamagnetic anions, 1[⊖] to 4[⊖]. The reaction sequence is formulated below for 3-H.



Results. - *Neutral radicals.* Figure 1 shows the ESR. spectra of the 1,6-methano-[11]annuleny1 (1·) and 1,6:8,14-propane-1,3-diylidene[15]annuleny1 (2·) radicals, while those of the benzotropy1 (3·) and 2,3-naphthotropy1 (4·) radicals are reproduced in Figure 2. As stated in the *Experimental Part*, the spectra of all four radicals were observed upon thermal dissociation of the respective dimer mixtures, (1)₂ to (4)₂, in high-boiling oil. The assignment of the proton coupling constants, $a_{\text{H}\mu}$, which are given in Table 1, has been based on the MO models (see Discussion). It was confirmed for the positions $\mu=9$ and 8,10 in 1· and for $\mu=6,8$ in 3· by studies of specifically deuteriated derivatives [6].

The temperature dependence of the equilibria $2 \times 1 \rightleftharpoons (1)_2$ to $2 \times 4 \rightleftharpoons (4)_2$ manifests itself in the intensities of the ESR. signals. The concentrations of the radicals, 1· to 4·, are expected to be proportional to the amplitudes of these signals,

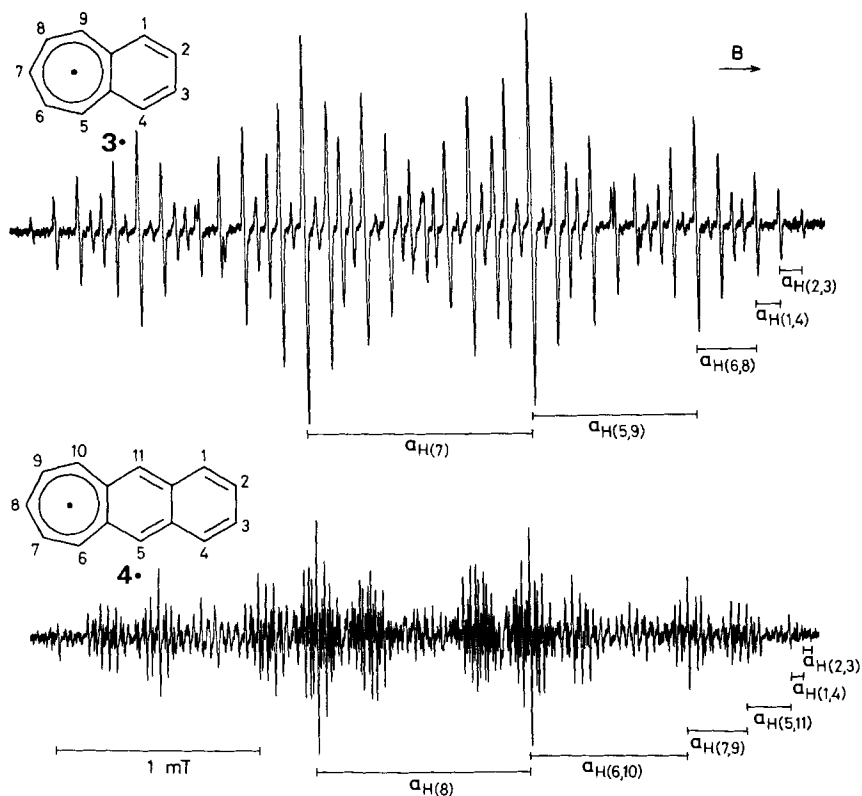


Fig. 2. ESR. spectra of the benzotropy1 (3·) and 2,3-naphthotropy1 (4·) radicals (Solvent: high-boiling oil; temperature: 423 K)

Table 1. Proton coupling constants, $a_{H\mu}$, in mT, for the 1,6-methano[11]annulenyl (1·), 1,6:8,14-propane-1,3-diylidene[15]annulenyl (2·), benzotropyyl (3·) and 2,3-naphthotropyyl (4·) radicals (Solvent: high-boiling oil)

Radical	1·		2·		3·		4·	
Temp. (K)	383		353		423		423	
	μ	$a_{H\mu}$	μ	$a_{H\mu}$	μ	$a_{H\mu}$	μ	$a_{H\mu}$
	2,5	0.437	2,5	0.356	1,4	0.118	1,4	0.062
	3,4	<0.005 ^{a)}	3,4	0.025	2,3	0.114	2,3	0.039
	7,11	0.638	7,15	0.472	5,9	0.816	5,11	0.213
	8,10	0.205 ^{b)}	9,13	0.495	6,8	0.299 ^{c)}	6,10	0.778
	9	0.764 ^{d)}	10,12	0.252	7	1.109	7,9	0.289
	12	{ 0.042 ^{e)} 0.021	11	0.609			8	1.042
			16	0.025				
			17	0.114 ^{f)}				
			18	0.025 ^{g)}				

^{a)} Unresolved in the ESR. spectrum (cf. Fig. 1). ^{b)} Replaced by $a_{D(8,10)} = 0.031$ mT in the ESR. spectrum of the 8,10-dideuterio-derivative. ^{c)} Replaced by $a_{D(6,8)} = 0.046$ mT in the ESR. spectrum of the 6,8-dideuterio-derivative. ^{d)} Replaced by $a_{D(9)} = 0.117$ mT in the ESR. spectrum of the 9-deuterio-derivative. ^{e)} Tentatively assigned to the methylene proton in the *exo*-position with respect to the 7,8,9,10,11-moiety of the cyclic π -system (cf. formula 1· in Fig. 1). ^{f)} Tentatively assigned to the methine proton in the *exo*-position with respect to the 9,10,11,12,13-moiety of the cyclic π -system (cf. formula 2· in Fig. 1). ^{g)} Two equivalent methylene protons (cf. formula 2· in Fig. 1).

if the line-widths and the line-shapes do not significantly alter in the temperature range of investigation. Such a condition was fulfilled for the most intensive hyperfine components of 1· to 4·, so that their amplitudes could be used as a measure of the relative concentrations, [1·] to [4·]. This information enabled one to determine the dissociation enthalpies, ΔH° , of the dimer mixtures by means of the *van't Hoff* equation

$$\frac{d \ln ([M\cdot]^2/[D])}{dT} = \frac{\Delta H^\circ}{RT^2}$$

or

$$2 \ln [M\cdot] - \ln [D] = -\frac{\Delta H^\circ}{RT} + \text{const.}$$

where D and M· stand for a dimer mixture, (1)₂ to (4)₂, and the corresponding monomeric radical, (1·) to (4·), respectively. (R and T have their usual meanings.) Since in our experiments the concentrations [D] greatly exceeded [M·], they were assumed to be constant. In fact, plots of $2 \ln [M\cdot]$ vs. $1/T$ yielded straight lines, the slopes of which were taken as equal to $-\Delta H^\circ/R$. The dissociation enthalpies, ΔH° , obtained in this way for (1)₂ to (4)₂ at temperatures between 253 and 423 K are listed in Table 2. In order to verify the reliability of the procedure, the ΔH° value of bitropyyl, which had previously been determined on pure dimer by *Vincow et al.* [8], was remeasured with bitropyyl dissolved in high-boiling oil, *i.e.*, under the same conditions as (1)₂ to (4)₂. It is evident from Table 2, in which the dissociation

Table 2. Dissociation enthalpies, ΔH° in kJ/mol, of bitropyyl and the dimers of 1,6-methano[11]annulenylyl, (1)₂, 1,6:8,14-propane-1,3-diylidene[15]annulenylyl, (2)₂, benzotropyyl, (3)₂, and 2,3-naphthotropyyl, (4)₂

Bitropyyl	(1) ₂	(2) ₂	(3) ₂	(4) ₂
139 ^a) (146) ^b)	102 ^a)	88 ^a)	136 ^a)	136 ^a)

^a) Experimental error ± 6 kJ/mol. ^b) Ref. [8]. Experimental error ± 4 kJ/mol.

enthalpies of bitropyyl obtained in both experiments are compared, that the previous result agrees with the present one within the limits of the sum of experimental errors (± 4 kJ/mol ± 6 kJ/mol = ± 10 kJ/mol).

Radical dianions. These studies are illustrated in Figure 3 by the ESR. spectra of the 1,6-methano[11]annulenylyl radical dianion (1[⊖]; counter-ions Na[⊕] and K[⊕]), and in Figure 4 by the ENDOR. spectra of 1[⊖] and its 9-deuterio- and 8,10-di-

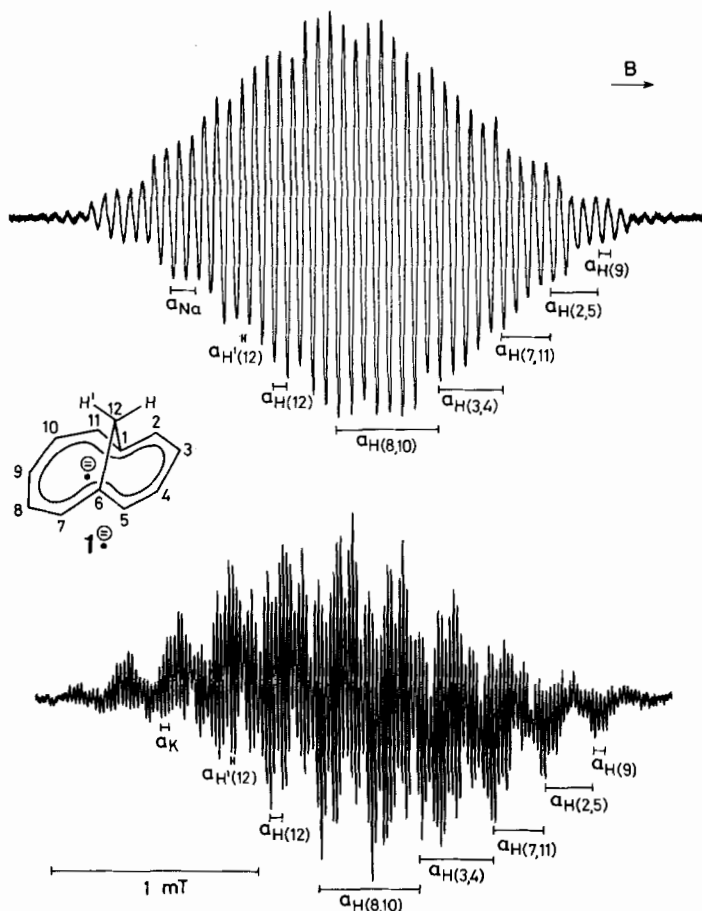


Fig. 3. ESR. spectra of the 1,6-methano[11]annulenylyl radical dianion (1[⊖]) (Solvent: DME; counter-ion: Na[⊕] (top) or K[⊕] (bottom); temperature: 193 K)

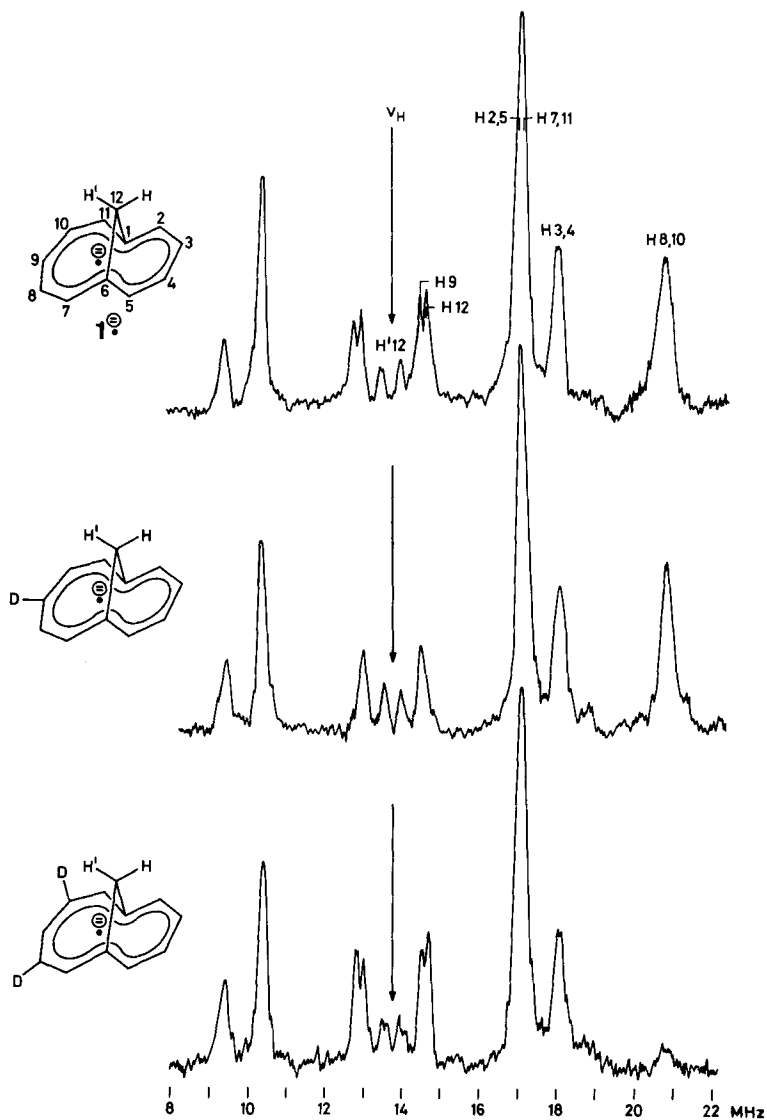


Fig.4. Proton ENDOR. spectra of 1,6-methano[11]annuleny radical dianion (1^{\ominus}) and its 9-deuterio- and 8,10-dideuterio-derivatives (Solvent: DME; counter-ion: Na^{\oplus} , temperature: 193 K)

deuterio-derivatives. The proton coupling constants, $a_{H\mu}$, for 1^{\ominus} and the radical dianions of 1,6:8,14-propane-1,3-diyldiene[15]annuleny (2^{\ominus}), benzotropy (3^{\ominus}) and 2,3-naphthotropy (4^{\ominus}) are listed in *Tables 3 and 4*. They do not markedly depend on the nature of the solvent (DME or THF) and on the temperature (183-273 K), but differ significantly with Na^{\oplus} and K^{\oplus} as the counter-ion. Those given in *Table 4* for 3^{\ominus} in DME (which also hold for this radical dianion in THF)

Table 3. Proton, ^{23}Na - and ^{39}K coupling constants, $a_{\text{H}\mu}$, a_{Na} and a_{K} in mT, for the 1,6-methano[11]-annulenyli (1^{\ominus}) and 1,6:8,14-propane-1,3-diylidene[15]annulenyli (2^{\ominus}) radical dianions (Solvent: DME; temperature: 193 K)

Radical dianion	1^{\ominus}			2^{\ominus}		
	μ	$a_{\text{H}\mu}$ Na^{\oplus}	K^{\oplus}	μ	$a_{\text{H}\mu}$ Na^{\oplus}	K^{\oplus}
Counter-ion	2,5	0.242	0.232	2,5	0.230	0.234
	3,4	0.310	0.357	3,4	0.269	0.278
	7,11	0.241	0.235	7,15	0.034	0.044
	8,10	0.499 ^{a)}	0.492 ^{a)}	9,13	0.165	0.169
	9	0.054 ^{b)}	0.058 ^{b)}	10,12	0.492 ^{c)}	0.485 ^{c)}
	12	{ 0.061 ^{d)}	{ 0.060 ^{d)}	11	0.076 ^{e)}	0.080 ^{e)}
		{ 0.016 ^{e)}	{ 0.017	16	<0.010 ^{f)}	<0.010 ^{f)}
				17	0.034 ^{g)}	0.038 ^{g)}
				18	0.034 ^{h)}	0.034 ^{h)}
	a_{Na}	0.115 ⁱ⁾			0.066 ⁱ⁾	
a_{K}		0.038 ⁱ⁾			0.039 ⁱ⁾	

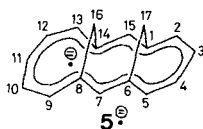
^{a)} Proton ENDOR. signals missing for the 8,10-dideuterio-derivative (cf. Fig. 4). Replaced by $a_{\text{D}(8,10)} = 0.076$ mT in the ESR. spectrum. ^{b)} Proton ENDOR. signals missing for the 9-deuterio-derivative (cf. Fig. 4). $a_{\text{D}(9)} = 0.009$ mT unresolved in the ESR. spectrum. ^{c)} Assignment supported by analogy with the $a_{\text{H}\mu}$ values for the 1,6:8,14-bismethano[15]annulenyli radical dianion (5^{\ominus}) and its 10,11,12-trideuterio-derivative (cf. Appendix 11). ^{d)} Tentatively assigned to the methylene proton in the *exo*-position with respect to the 7,8,9,10,11-moiety of the cyclic π -system (cf. formula 1^{\ominus} in Fig. 3). ^{e)} Hyperfine splitting unresolved in the ESR. spectrum (cf. Fig. 3). Determined from the ENDOR. signals (cf. Fig. 4). ^{f)} Unresolved in the ESR. spectrum. Estimated from proton ENDOR. signals. ^{g)} Tentatively assigned to the methine proton in the *exo*-position with respect to the 9,10,11,12,13-moiety of the cyclic π -system (cf. formula 2- in Fig. 1). ^{h)} Two equivalent methylene protons (cf. formula 2- in Fig. 1). ⁱ⁾ One nucleus of a counter-ion.

Table 4. Proton, ^{23}Na - and ^{39}K coupling constants, $a_{\text{H}\mu}$, a_{Na} and a_{K} in mT, for the benzotrotyl (3^{\ominus}) and 2,3-naphthotrotyl (4^{\ominus}) radical dianions (Solvent: DME; temperature: 193 K)

Radical dianion	3^{\ominus}			4^{\ominus}			
	μ	$a_{\text{H}\mu}$ Na^{\oplus}	K^{\oplus}	μ	$a_{\text{H}\mu}$ Na^{\oplus} ^{a)}	K^{\oplus}	
Counter-ion	1,4	<0.006 ^{b)}	<0.006 ^{b)}	1,4	<0.006 ^{b)}	0.100 ^{b)}	
	2,3	0.260	0.271	2,3	0.125 ^{c)}	0.128 ^{c)}	
	5,9	0.129	0.115	5,11	0.045 ^{c)}	0.056 ^{c)}	
	6,8	0.627 ^{d)}	0.625 ^{d)}	6,10	0.136	0.139	
	7		0.079	0.075	7,9	0.589 ^{e)}	0.595 ^{e)}
					8	0.082	0.089
	a_{Na}	0.107 ^{f)}			^{a)}		
a_{K}		0.039 ^{f)}			0.038 ^{f)}		

^{a)} Poorly resolved ESR. spectrum. All values $a_{\text{H}\mu}$ from the proton ENDOR. signals; a_{Na} not determined. ^{b)} Unresolved in the ESR. spectrum. Estimated from proton ENDOR. signals. ^{c)} Proton ENDOR. signals missing for the 1,2,3,4,5,11-hexadeuterio-derivative. Poorly resolved ESR. spectrum of this derivative. ^{d)} Proton ENDOR. signals missing for the 6,8-dideuterio-derivative. Replaced by $a_{\text{D}(6,8)} = 0.096$ mT in the ESR. spectrum. ^{e)} Proton ENDOR. signals missing for the 7,9-dideuterio-derivative. Replaced by $a_{\text{D}(7,9)} = 0.091$ mT in the ESR. spectrum with K^{\oplus} as the counter-ion. ^{f)} Two equivalent nuclei of the counter-ions.

indicate that the previous analysis of the ESR. spectrum of 3^{\ominus} [7] was not entirely correct. Just as for the corresponding neutral radicals, the assignment has been based on MO models and was corroborated for the positions $\mu=9$ or $8, 10$ in 1^{\ominus} and for $\mu=6, 8$ in 3^{\ominus} by studies of specifically deuteriated derivatives. In addition, it was possible²⁾ to examine the ESR.- and ENDOR. spectra of 4^{\ominus} deuteriated in the positions $\mu=7, 9$ or $1, 2, 3, 4, 5, 11$ and thus to provide a check of the assignment of the $a_{H\mu}$ values for this radical dianion [6]. Moreover, investigations were carried out on the radical dianion of 1,6:8,14-bismethano[15]annulenyI (5^{\ominus}) and its 10, 11, 12-trideuterio-derivative. Since 5^{\ominus} is structurally closely related to 2^{\ominus} , the results of these investigations (see *Appendix II*) could be used to confirm the assignment to the analogous positions μ in 2^{\ominus} .



It is interesting to note that hyperfine splittings from two equivalent ^{23}Na or ^{39}K nuclei of the counter-ions were observed in the ESR. spectra of 3^{\ominus} and 4^{\ominus} ³⁾, whereas in the case of 1^{\ominus} and 2^{\ominus} those from only one such nucleus appeared. Presumably, splittings due to a second ^{23}Na or ^{39}K nucleus are too small to be resolved, so that their presence was revealed merely by increased line-widths.

Discussion. - *MO models.* A convenient starting point for an MO description of the π -systems considered in the present paper are 11- and 15-membered π -perimeters. Since the bonding perimeter MO's are fully occupied in the cations, the unpaired electron in the radicals and the radical dianions must enter one of the antibonding MO's. *Figure 5* depicts the degenerate pair of the lowest antibonding MO's of the 11- and 15-membered perimeters. The shapes of these perimeters have been adapted to the outer C-frameworks of benzo- and 2,3-naphthotropyI, respectively, and thus they resemble the cyclic C-skeletons of the corresponding bridged [11]- and [15]annulenyIs. In each π -perimeter (symmetry C_{2v}), the two MO's have been classified as symmetric (ψ_S) or antisymmetric (ψ_A) with respect to the mirror plane (m) which is perpendicular to the plane of the π -system. In the simplest models such as HMO, which allow only for interactions between bonded centres, the lowering of the symmetry of the perimeters from D_{11h} or D_{15h} to C_{2v} leaves the degeneracies of ψ_S and ψ_A unaffected. These degeneracies are removed in the π -systems of benzotropyI and 2,3-naphthotropyI by formation of one and two cross-bonds, respectively. As pointed out by the absolute values and relative signs of the LCAO-coefficients at the centres linked by these bonds, the MO's ψ_S should be slightly stabilized and their counterparts ψ_A strongly destabilized (*Fig. 5*).

- 2) Since the studies of the radical dianions required less material than those of the neutral radicals, they could be performed even on very small quantities available for some deuteriated compounds.
- 3) The observation of ^{23}Na hyperfine splittings in the ESR. spectrum of 4^{\ominus} with Na^{\oplus} as the counter-ion was prevented by the poor resolution (*cf.* footnote a to *Table 4*).

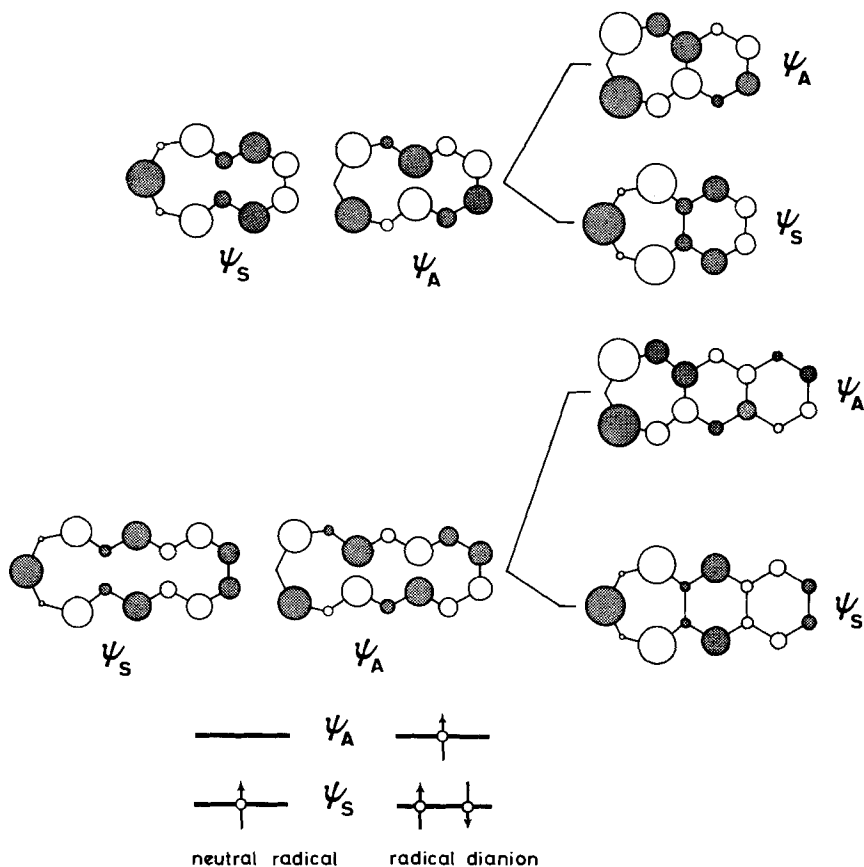


Fig. 5. Degenerate lowest antibonding orbitals, ψ_S and ψ_A , of the 11- and 15-membered π -perimeters, and removal of the degeneracy by cross-linking to give benzotropyl and 2,3-naphthotropyll π -systems (The areas of the circles are proportional to the squares of the LCAO-coefficients. Blank and dotted areas symbolize opposite signs of these coefficients). Bottom: Predicted occupancy of ψ_S and ψ_A in the neutral radicals and radical dianions.

In the bridged [11]- and [15]annulenylys, several types of perturbations have to be examined, namely 1) the inductive and hyperconjugative effects of the bridging alkylidene groups, 2) the homoconjugative interactions between the formally non-bonded, but spatially proximate bridged centres, and 3) the distortions of the cyclic π -systems from planarity. Of these perturbations, it is for our purpose (removal of the degeneracy of the MO's ψ_S and ψ_A) sufficient to consider the inductive effect and the homoconjugative interactions. Neglect of hyperconjugation is justified, because the LCAO-coefficients in the MO's ψ_S exhibit only small absolute values at the bridged centres, while the MO's ψ_A are not affected at all for symmetry reasons (mirror plane m =nodal plane). Distortions from planarity may be disregarded, in view of their relatively slight effect on the energies of the MO's ψ_S and ψ_A , as indicated by a first-order perturbation calculation which makes use

of the twist angles determined by X-ray crystallography of the cations 1^{\oplus} [3d] [9a] and 5^{\oplus} [9b]⁴). (See [10] for an analogous calculation in the series of 1,6:8,13-bridged [14]annulenes.)

According to the absolute values of the LCAO-coefficients at the bridged centres, the inductive effect should raise the energies of the MO's ψ_A much more strongly than those of ψ_S . The homoconjugative interactions are expected to work in the same directions as the cross-bonding, albeit to a lesser extent. The energy sequence, the MO's ψ_A above ψ_S , which applies to benzo- and naphthotropyyl π -systems, is thus predicted also for the bridged [11]- and [15]annulenyls in terms of both inductive and homoconjugative effects. As a consequence, the singly occupied orbitals in the neutral radicals, $1\cdot$ to $4\cdot$, ought to resemble the symmetric MO's ψ_S , whereas those in the radical dianions, 1^{\ominus} to 4^{\ominus} , have to be of the anti-symmetric ψ_A -type (Fig. 5). This means that the π -spin distributions in the paramagnetic species of the annulenyl series are not expected to differ fundamentally from those in the benzo- and naphthotropyyl analogues. The conclusions drawn with respect to the contributions of homotropyyl structures to the π -systems of the radicals and radical dianions of the bridged [11]- and [15]annulenyls are therefore less straightforward than they might be in the case where the inductive effect of the bridging alkylidene groups and the interactions between the bridged centres would shift the energies of the degenerate perimeter MO's in opposite directions.

π -Spin distributions. The hyperfine data for the radicals, $1\cdot$ to $4\cdot$ (Table 1), as well as those for the radical dianions, 1^{\ominus} to 4^{\ominus} (Tables 3 and 4), are in accord with the predictions of the simple model. As expected for the single occupancy of a ψ_S -like orbital, the largest coupling constants $a_{H\mu}$ (0.6 to 1.1 mT) observed for the neutral radicals belong to the protons at the centres μ , which are situated in the mirror plane m ($\mu=9$ in $1\cdot$, 11 in $2\cdot$, 7 in $3\cdot$, and 8 in $4\cdot$). On the other hand, the corresponding $a_{H\mu}$ values are rather small for the radical dianions (0.05 to 0.09 mT) and are thus consistent with m being the nodal plane of the singly occupied ψ_A -like orbital. Also in line with such an occupancy is the finding that the largest coupling constants $a_{H\mu}$ for the radical dianions (0.48 to 0.63 mT) arise from pairs of equivalent protons at the centres μ which are adjacent to the one situated in the plane m ($\mu=8, 10$ in 1^{\ominus} , 10, 12 in 2^{\ominus} , 6, 8 in 3^{\ominus} , and 7, 9 in 4^{\ominus}).

A thorough interpretation of the hyperfine data for the radicals and radical dianions of the bridged [11]- and [15]annulenyls in terms of π -spin distributions is somewhat impaired by the non-planarity of their perimeters, because distortions of such cyclic π -systems from planarity can seriously affect the coupling constants of the ring protons, as a result of a break-down of the σ - π -separation [11]. Since it is difficult to estimate the effect of non-planarity on the $a_{H\mu}$ values for $1\cdot$, $2\cdot$, 1^{\ominus} and 2^{\ominus} , an attempt has been made to discuss these proton hyperfine data without taking such an effect into account. The procedure used is exemplified below on the 1,6-methano[11]annulenyl radical ($1\cdot$).

In Figure 6, the absolute values $|\rho_{\mu}|$ of the π -spin populations, which were calculated by the *McLachlan* method [12] ($\lambda=1.2$) for the single occupancy of

⁴) The X-ray crystallographic data for 5^{\oplus} were taken as a substitute for those of 2^{\oplus} .

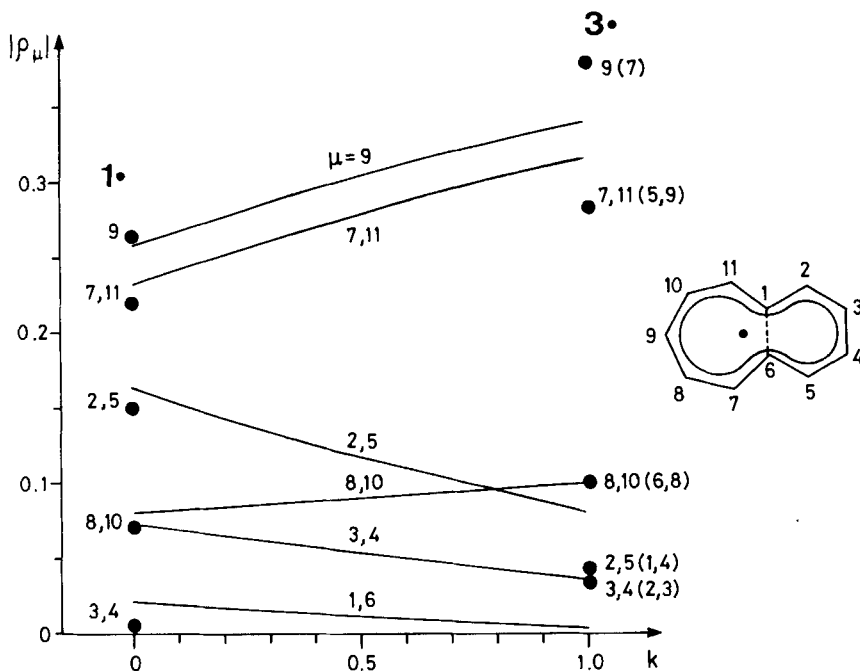


Fig. 6. Calculated π -spin populations $|\rho_\mu|$ in the [11]annulenyl radical as a function of the parameter k of the bond integral $\beta_{16} = k\beta$ (The values $|\rho_\mu|$ are the means of those obtained using the polarizabilities $\pi_{\mu\nu}$ of the cation and the anion [12]. The filled circles represent the 'experimental' π -spin populations in the 1,6-methano[11]annulenyl (1 \cdot) and benzotropyyl (3 \cdot) radicals. The numbers in parentheses are the conventional ones for the positions μ in 3 \cdot)

MO ψ_S in the 11-membered perimeter, are plotted vs. the parameter k defined by $\beta_{16} = k\beta$, where β_{16} is the bond integral of the cross-link C(1)–C(6). (The numbering of the C-centres μ follows that of 1,6-methano[11]annulenyl.) The parameters $k=0$ and 1 refer to the π -system of an unperturbed [11]annulenyl and benzotropyyl, respectively, while $k \approx 0.5$ [13] would be appropriate for a homotropyyl structure. It is evident from Figure 6 that, on going from $k=0$ to 1, the $|\rho_\mu|$ values increase at the centres $\mu=7$ to 11, which make part of the formed 7-membered ring, and decrease at the remaining centres $\mu=1$ to 6. The cross-linking C(1)–C(6), which leads from [11]annulenyl to benzotropyyl radical, is thus predicted to give rise to a more pronounced π -spin localization on the proton-bearing centres of the 7-membered ring. In order to compare the calculated $|\rho_\mu|$ values with the hyperfine data for 1,6-methano[11]annulenyl (1 \cdot) and benzotropyyl (3 \cdot) radicals, the observed proton coupling constants, $a_{H\mu}$, were converted into 'experimental' π -spin populations $|\rho_\mu|$ by means of the McConnell equation $a_{H\mu} = Q \cdot \rho_\mu$ [14] with the proportionality factor $|Q| = 2.9 \text{ mT}^5$). Such 'experimental' $|\rho_\mu|$ values for the proton-

5) The $|Q|$ value of 2.9 mT seems appropriate for neutral radicals with extended π -systems and substantial negative π -spin populations ρ_μ ; see, e.g., [15] for phenalenyl.

bearing centres $\mu=2$ to 5 and 7 to 11 are inserted in *Figure 6*. It is evident that the predicted changes in the π -spin populations $|\rho_\mu|$ by increasing k from 0 to 1 are reflected by their experimental counterparts on passing from $\mathbf{1}\cdot$ to $\mathbf{3}\cdot$. It thus appears that satisfactory agreement between theory and experiment for $\mathbf{1}\cdot$ requires the use of a rather small value of k (<0.4). Analogous treatment of the remaining pairs of paramagnetic species in the two series, $\mathbf{2}\cdot$ vs. $\mathbf{4}\cdot$, $\mathbf{1}^\ominus$ vs. $\mathbf{3}^\ominus$, and $\mathbf{2}^\ominus$ vs. $\mathbf{4}^\ominus$ leads to a similar statement with respect to the parameter k .

π -Delocalization energies of the radicals. Whereas the dissociation enthalpies, ΔH° , of bitropyl and the dimers, $(\mathbf{3})_2$ and $(\mathbf{4})_2$, of benzo- and naphthotropyl only slightly differ from each other, a considerable decrease is found on going from bitropyl to the dimers $(\mathbf{1})_2$ and $(\mathbf{2})_2$ of the bridged [11]- and [15]annulenyls (*Table 2*). Since the dimerization of $\mathbf{1}\cdot$, $\mathbf{2}\cdot$ and $\mathbf{4}\cdot$, like that of $\mathbf{3}\cdot$ (*cf. Exper. Part*), ought to occur at the three centres bearing the highest π -spin populations ρ_μ ($\mu=7,9,11$ in $\mathbf{1}\cdot$, 9,11,13 in $\mathbf{2}\cdot$, 5,7,9 in $\mathbf{3}\cdot$, and 6,8,10 in $\mathbf{4}\cdot$), the steric factors should not greatly differ for the cleavage of the central single bond in the dimers under consideration. Assuming that other factors, such as the inherent energy of this bond and rehybridization of the C-atoms involved, are also nearly equal throughout the series, the observed decrease in the ΔH° values of $(\mathbf{1})_2$ and $(\mathbf{2})_2$ relative to bitropyl, $(\mathbf{3})_2$ and $(\mathbf{4})_2$ implies an increased gain in π -electron delocalization energy upon dissociation. Obviously, such a gain is little affected by the benzo- and 2,3-naphtho-annelation of the cyclic π -system of tropyl, but it is markedly enlarged when the tropyl π -system is extended to those 1,6-methano[11]-annulenyl and 1,6:8,14-propane-1,3-diyliene[15]annulenyl. As compared with $\mathbf{3}\cdot$ and $\mathbf{4}\cdot$, the radicals $\mathbf{1}\cdot$ and $\mathbf{2}\cdot$ must thus exhibit an additional 'resonance stabilization' energy, due to the π -electron delocalization over the entire 11- and 15-membered π -perimeters. In this respect, it is interesting to note that analogous results for annulenes are scarce; no significant increase in the resonance stabilization energy was derived for [18]annulene relative to benzene [16].

The interpretation of the observed differences in the dissociation enthalpies in terms of differing gains in π -delocalization energies, $\Delta(DE)_\pi$, is in line with the simplest MO model which treats the radicals $\mathbf{1}\cdot$ and $\mathbf{2}\cdot$ as unperturbed 11- and 15-membered π -perimeters, respectively. This model yields the following $\Delta(DE)_\pi$ values (in β -units): 3.09 for bitropyl $\rightarrow 2 \times$ tropyl; 3.51 for bis[11]annulenyl $\rightarrow 2 \times$ [11]annulenyl; 3.58 for bis[15]annulenyl $\rightarrow 2 \times$ [15]annulenyl; 3.21 for bis(benzotropyl) $\rightarrow 2 \times$ benzotropyl, and 3.10 for bis(2,3-naphthotropyl) $\rightarrow 2 \times$ (2,3)naphthotropyl. From these values and the observed dissociation enthalpies, ΔH° , for the dimer mixtures, $(\mathbf{1})_2$ to $(\mathbf{4})_2$ (*Table 2*), an estimate of 100 kJ/mol is obtained for the bond integral $|\beta|$.

The occurrence of the dimers, $(\mathbf{1})_2$ to $(\mathbf{4})_2$, as mixtures of isomers did not complicate the HMO calculations for the [11]- and [15]annulenyls, since all their dimers are identical in the simplest model. For benzotropyl the weighted mean of the delocalization energies of $(\mathbf{3}')_2$, $(\mathbf{3}'')_2$ and $(\mathbf{3}''')_2$ was used as found by ^{13}C -NMR spectroscopy (ratio 8:1:1; see *Exper. Part*), and an analogous treatment was applied to 2,3-naphthotropyl, the dimer mixture of which was assumed to consist of the corresponding isomers, $(\mathbf{4}')_2$, $(\mathbf{4}'')_2$ and $(\mathbf{4}''')_2$, in the same concentration ratio.

Ion pairs formed by the radical dianions with alkali metal cations. As indicated by relatively large ^{23}Na or ^{39}K hyperfine splittings in the ESR spectra, the radical

dianions, 1^{\ominus} to 4^{\ominus} , tightly associate with their counter-ions Na^{\oplus} or K^{\oplus} in ethereal solvents DME or THF. The different numbers of equivalent alkali metal nuclei, which give rise to such splittings, one for 1^{\ominus} and 2^{\ominus} , and two for 3^{\ominus} and 4^{\ominus} , are readily understood. It can be reasonably expected that in the ion pairs of benzotropyyl (3^{\ominus}) and 2,3-naphthotropyyl (4^{\ominus}) radical dianions each of the two counter-ions occupies an equivalent site above or below the molecular plane, presumably close to the 7-membered ring bearing the bulk of the two negative charges. On the other hand, in the ion pairs of 1,6-methano[11]annulenyyl (1^{\ominus}) and 1,6:8,14-propane-1,3-diylidene[15]annulenyyl (2^{\ominus}) only the counter-ion situated under the bridge can properly interact with the doubly charged π -perimeter, whereas a tight association of the second cation is impeded by the bridging group. The suggested structures of the ion pairs are shown in Figure 7 for 1^{\ominus} and 3^{\ominus} .

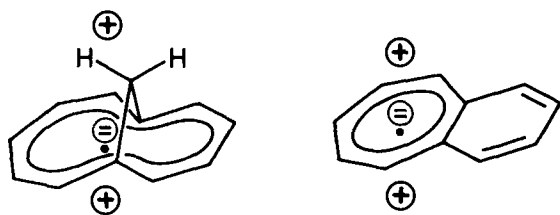


Fig. 7. Schematic representation of the presumed locations of the alkali metal cations associated with the 1,6-methano[11]annulenyyl (1^{\ominus}) (left) and benzotropyyl (3^{\ominus}) (right) radical dianions

Conclusions. - The additional 'resonance stabilization' energies of the bridged [11]- and [15]annulenylys support the currently used formulae $1\cdot$ and $2\cdot$, which suggest a cyclic π -electron delocalization over the entire 11- and 15-membered perimeters. Moreover, the differences in the coupling constants, $a_{\text{H}\mu}$, on passing from $1\cdot$, $2\cdot$, 1^{\ominus} and 2^{\ominus} to their benzo- and naphthotropyyl analogues, $3\cdot$, $4\cdot$, 3^{\ominus} and 4^{\ominus} , can be interpreted in terms of simple perimeter models without explicitly allowing for a substantial homoconjugative interaction between the bridged centres. However, in view of the crudeness of the models, too much significance should not be paid to this outcome. In particular, it would be presumptuous to state that the contributions of the homotropyyl structures $1a\cdot$, $2a\cdot$, $1a^{\ominus}$ and $2a^{\ominus}$ to the π -systems $1\cdot$, $2\cdot$, 1^{\ominus} and 2^{\ominus} are negligible. The most serious handicaps in the interpretation of the $a_{\text{H}\mu}$ values are 1) the experimental inseparability of the inductive and homoconjugative effects on the energies of the lowest antibonding orbitals ψ_{S} and ψ_{A} , and 2) the difficulty to assess reliably the consequences of the distortions of the cyclic π -systems from planarity. These handicaps could be obviated by the use of suitable reference π -systems, in addition to $3\cdot$, $4\cdot$, 3^{\ominus} and 4^{\ominus} . Unfortunately, such systems are unavailable at present.

Appendix I. - As stated in the *Exper. Part*, reaction of 7H-benzocycloheptene (3-H) and 6H-(2,3-naphtho)cycloheptene (4-H) with Na or K in DME or THF yielded the radical dianions of benzotropyyl (3^{\ominus}) and 2,3-naphthotropyyl (4^{\ominus}), respectively, as the final products. The primarily formed radical anions (3-H^{\ominus}) and (4-H^{\ominus}) were also characterized by ESR. and ENDOR. spectroscopy. The pertinent proton coupling constants, $a_{\text{H}\mu}$ (for numbering see formulae in *Exper. Part*), are listed in Table 5. Their assignment has been made by correlating them with the π -spin populations $|\rho_{\mu}|$ calculated according to the *McLachlan* procedure [12]. A partial experimental confirmation of this assignment was provided by specific deuteriations in the position $\mu=7$ for (3-H^{\ominus}) and in $\mu=1,2,3,4,5,11$ for (4-H^{\ominus}).

Table 5. Proton coupling constants, $a_{H\mu}$ in mT, for the radical anions of 7H-benzocycloheptene, (3-H) $^{\ominus}$, and 6H-(2,3-naphtho)cycloheptene, (4-H) $^{\ominus}$ (Solvent: DME, temperature: 193 K, counter-ion: K $^{\oplus}$)

Radical anion	(3-H) $^{\ominus}$		(4-H) $^{\ominus}$			
	μ	$a_{H\mu}$	μ	$a_{H\mu}$	μ	$a_{H\mu}$
	1,4	0.018	1	0.450 ^{a)}	7	0.346
	2,3	0.304	2	0.082 ^{a)}	8	0.107
	5,9	0.036	3	0.250 ^{a)}	9	0.214
	6,8	0.625	4	0.332 ^{a)}	10	0.046
	7	0.190 ^{b)c)}	5	0.419 ^{a)}	11	0.533 ^{a)}
			6	0.011 ^{b)}		

a) Proton ENDOR. signals missing for the 1,2,3,4,5,11-hexadeuterio-derivative. Poorly resolved ESR. spectrum of this derivative. b) Two equivalent methylene protons. c) Proton ENDOR. signal missing for the 7,7-dideuterio-derivative. Replaced by $a_{D(7)} = 0.029$ mT in the ESR. spectrum.

Appendix II. - The radical dianion of 1,6:8,14-bismethano[15]annuleny (5 $^{\ominus}$) was prepared in an analogous way to that of the propane-bridged [15]annuleny (2 $^{\ominus}$) (*cf. Exper. Part*). The ESR. and ENDOR. spectra of 5 $^{\ominus}$ in DME (counter-ion K $^{\oplus}$) yielded the following proton coupling constants, $a_{H\mu}$ in mT (for the numbering of positions μ see formula in the *Results*):

μ	2,5	3,4	7,15	9,13	10,12	11	16	17
$a_{H\mu}$	0.286	0.319	0.035	0.185	0.441	0.067	0.097 } 0.035 }	0.185 } 0.035 }

The assignment of the $a_{H\mu}$ values to the ring protons ($\mu = 2$ to 5, 7, and 9 to 13) corresponds to that made for 2 $^{\ominus}$ (Table 3). It was confirmed for $\mu = 10, 12$ and 11 by the study of the 10,11,12-trideuteriated derivative. For the four methylene protons, the assignment of the $a_{H\mu}$ values ($\mu = 16$ and 17) is tentative.

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