

282. Radical Ions in the Pentalene Series [1]. Part II. Dibenzo [*b, f*]pentalene¹⁾ and its 5,10-Dimethyl Derivative

by Peter Fürderer and Fabian Gerson

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

and Mordecai Rabinovitz and Itamar Willner

Department of Organic Chemistry, The Hebrew University of Jerusalem,
Jerusalem, Israel

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Summary

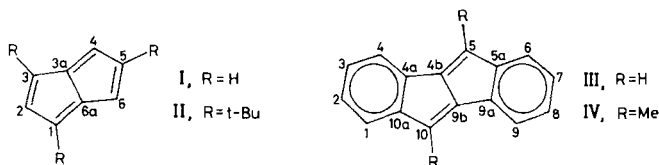
Proton hyperfine data have been determined for the radical anions and cations of dibenzo [*b, f*]pentalene (III) and its 5,10-dimethyl derivative (IV). The assignment of the coupling constants to pairs of equivalent protons follows from a simple MO model, the use of which enables one to reproduce satisfactorily the experimental values. The proton hyperfine data, $a_{\text{H}\mu}$ ²⁾, for the radical anion III[⊖] correlate fairly well with the π -charge populations ε_{μ} derived from ¹H-NMR. spectra for the carbon centres μ in the dianion III^{2⊖}. The analogous correlation is less good in the case of the radical cation III[⊕] and the dication III^{2⊕}, presumably due to the rough approximations involved in the evaluation of the numbers ε_{μ} for the latter species. The coupling constants $a_{\text{H}5,10}$ for III[⊖] and III[⊕] are very close to the corresponding values $a_{\text{H}4,6}$ for the radical ions of 1,3,5-tri-*t*-butylpentalene (II), in accord with the prediction of the MO model. A similarity is also found between the proton hyperfine data for III[⊖] and those for the radical anions of structurally related 1,4-diphenyl-1,3-butadiene (V). On the other hand, there are striking changes in the coupling constants of the analogous protons on passing from III[⊖] to the radical anions of dibenzo [*a, e*]cyclooctene (VI) and [16]annulene (VII), as a consequence of raising the symmetry from C_{2h} to D_{2h} and D_{4h} , respectively.

Introduction. – In the preceding paper of this series [1], we have reported the complete hyperfine data for the radical ions of 1,3,5-tri-*t*-butylpentalene (II), a stable alkyl derivative of pentalene (I). Recently, the dianions and the dications of dibenzo [*b, f*]pentalene (III) and its 5,10-dimethyl derivative (IV) have been prepared in solution and studied by ¹H- and ¹³C-NMR. spectroscopy [2]. Based on the ‘diatropicity’ of III^{2⊖}, IV^{2⊖}, III^{2⊕} and IV^{2⊕}, an ‘aromatic’ character has been ascribed to these $(4n+2)$ π -electron systems, in contrast to the ‘anti-aromaticity’ of

¹⁾ The IUPAC name for dibenzo [*b, f*]pentalene (III) is indeno[2,1-*a*]indene.

²⁾ The meaning of $a_{\text{H}\mu}$ is $a_{\text{H}-\text{C}(x),\text{H}-\text{C}(y)}$, whereas only x and y are given in the particular cases.

the neutral compounds, III and IV, containing $4n$ π -electrons. In the present paper, we describe the ESR. spectra of the radical anions III^{\ominus} and IV^{\ominus} , and of the radical cations III^{\oplus} and IV^{\oplus} , which represent the intermediate π -electron systems. The proton coupling constants for III^{\ominus} and III^{\oplus} are compared with the π -charge populations at the carbon centres of the dianion $\text{III}^{2\ominus}$ and the dication $\text{III}^{2\oplus}$ [2b], respectively, as well as with the hyperfine data for the radical ions of the pentalene derivative II [1] [3] and of some alternant hydrocarbons structurally related to III.



Experimental Part. - Dibenzo[*b,f*]pentalene (III), and its 5,10-dimethyl derivative (IV), were prepared according to procedures given in the literature (III: [4]; IV: [5]).

The radical anions III^{\ominus} and IV^{\ominus} were produced from the respective neutral compounds by reaction with potassium in 1,2-dimethoxyethane (DME) and by electrolytic reduction in dimethylformamide (DMF) containing tetraethylammonium perchlorate as the supporting salt. Oxidation of the compounds with aluminium trichloride in methylene chloride yielded the corresponding radical cations III^{\oplus} and IV^{\oplus} . Under these conditions, formation of III^{\ominus} , IV^{\ominus} and IV^{\oplus} proceeded quite readily at low temperatures, whereas III^{\oplus} could be generated only above 243 K. The resulting radical ions were less stable in the case of the unsubstituted dibenzo[*b,f*]pentalene (III) than in that of the 5,10-dimethyl derivative (IV); their half-lives varied from 15 min to several hours in the temperature range between 183 and 273 K.

The g -factors were 2.0026 ± 0.0001 for the radical anions III^{\ominus} and IV^{\ominus} , and 2.0025 ± 0.0001 for the corresponding cations III^{\oplus} and IV^{\oplus} .

Results. - *Figure 1* shows the ESR. spectra of the radical anions III^{\ominus} and IV^{\ominus} in DME at 183 K with K^{\oplus} as the counterion. The spectra of the radical cations III^{\oplus} and IV^{\oplus} in methylene chloride, at 273 and 243 K, respectively, are reproduced in *Figure 2*. The hyperfine patterns of III^{\ominus} and III^{\oplus} are readily analyzed in terms of five coupling constants, $a_{\text{H}\mu}$, each for two equivalent protons, while for IV^{\ominus} and IV^{\oplus} a splitting due to six equivalent protons is found, in addition to four two-proton values $a_{\text{H}\mu}$. The pertinent data are given in *Table 1*; in the case of III^{\ominus} and IV^{\ominus} , they comprise also the coupling constants observed with the solvent DMF and the counterion $\text{Et}_4\text{N}^{\oplus}$ at 213 K. Only the splitting from the six protons in the two methyl 5,10-substituents of IV^{\ominus} and IV^{\oplus} could be assigned straightforwardly by its multiplicity in the ESR. spectra. The assignment of the remaining coupling constants $a_{\text{H}\mu}$ to pairs of equivalent protons at the individual centres μ of III^{\ominus} , III^{\oplus} , IV^{\ominus} and IV^{\oplus} is based on MO calculations (see below).

Discussion. - *Assignment of the coupling constants.* Together with the experimental data, *Table 1* lists the values $a_{\text{H}\mu}$ obtained for the radical ions of dibenzo[*b,f*]pentalene (III) with the use of the *McConnell* relation [6] in which the π -spin populations ρ_{μ} at the proton bearing centres μ were calculated by means of the *McLachlan* procedure ($\lambda = 1.0$) [7]. For the parameter Q the same values, -2.4 (III^{\ominus}) and -2.8 mT (III^{\oplus}), have been adopted as those employed previously [1]

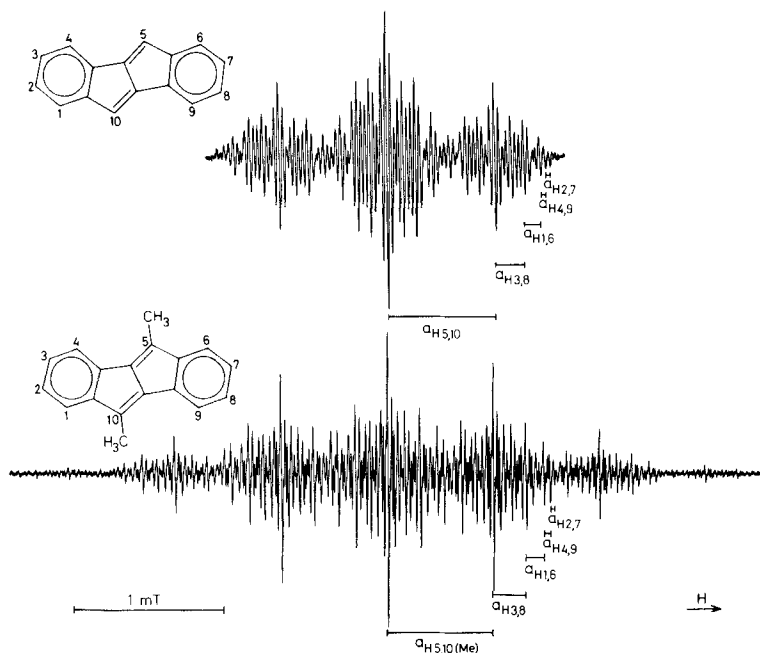


Fig. 1. ESR. spectra of the radical anions of dibenzo[b,f]pentalene (III) and its 5,10-dimethyl derivative (IV) (Solvent: DME; counterion: K^{\oplus} ; temp.: 183 K)

in the case of the radical anion and cation of 1,3,5-tri-*t*-butylpentalene (II). The good agreement between the observed and calculated values $|a_{H\mu}|$ justifies the assignment of the experimentally found five coupling constants for III^{\ominus} and III^{\oplus} . The four two-proton values $a_{H\mu}$ for IV^{\ominus} and IV^{\oplus} are assigned by analogy, since methyl substitution does not, in general, strongly affect the π -spin distribution in extended radical ions with a non-degenerated ground state [8]. For the protons at the 5,10-centres of III^{\ominus} and III^{\oplus} , the assignment is substantiated by comparison of the pertinent value $a_{H5,10}$ with the coupling constant, $a_{H5,10(Me)}$, of the six methyl protons in IV^{\ominus} and IV^{\oplus} . The ratios $|a_{H5,10(Me)}|/|a_{H5,10}|$, which amount to 0.712 mT/0.722 mT ≈ 1 for IV^{\ominus} and III^{\ominus} , and to 0.068 mT/0.033 mT ≈ 2 for IV^{\oplus} and III^{\oplus} , are in line with the analogous numbers $|a_{H\mu(Me)}|/|a_{H\mu}|$ found for the coupling constants upon methyl substitution of the radical anions and cations, respectively [8]. The best known example in this regard is provided by the radical ions of anthracene [9] and its 9,10-dimethyl derivative [10].

Comparison with the diions. In Table 2 the coupling constants, $a_{H\mu}$, for the radical anion III^{\ominus} and the radical cation III^{\oplus} are given along with the π -charge populations ε_{μ} which were determined from the chemical shifts in the 1H -NMR. spectra for the proton bearing centres μ of the dianion $III^{2\ominus}$ and the dication $III^{2\oplus}$ [2b]. The correlation between the values $a_{H\mu}$ and ε_{μ} is fairly good in the case of III^{\ominus} and $III^{2\ominus}$, whereas in that of III^{\oplus} and $III^{2\oplus}$ it leaves much to be desired. The rather poor agreement in the latter case must be due to the very approximate nature of the π -

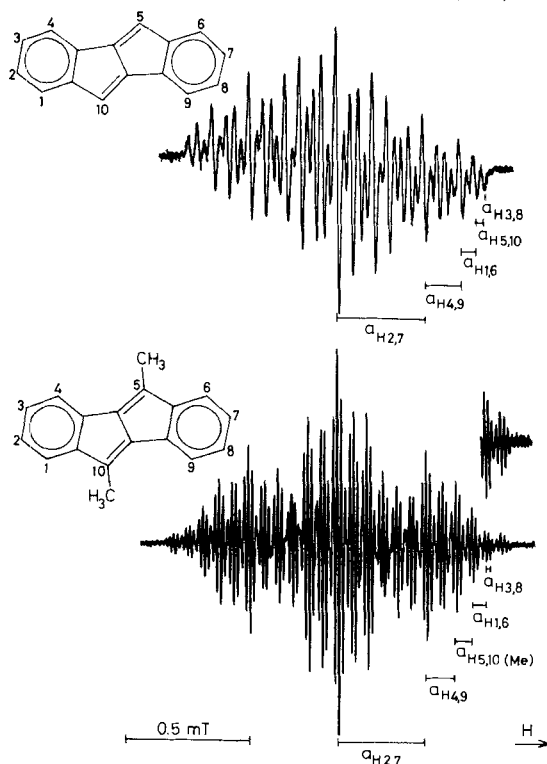


Fig. 2. ESR. spectra of the radical cations of dibenzo[b,f]pentalene (III) and its 5,10-dimethyl derivative (IV) (Solvent: CH_2Cl_2 ; temp.: 273 (III $^{\oplus}$) and 243 K (IV $^{\oplus}$))

Table 1. Proton coupling constants, $a_{\text{H}\mu}$ ^{a)} in mT, for the radical ions of dibenzo[b,f]pentalene (III) and its 5,10-dimethyl derivative (IV)

μ	$a_{\text{H}\mu}$, observed ^{b)}				$a_{\text{H}\mu}$, calculated			
	III $^{\ominus}$		IV $^{\ominus}$		III $^{\oplus}$		IV $^{\oplus}$	
	c)	d)	e)	f)	g)	h)	i)	j)
1,6	0.109	0.111	0.117	0.123	0.058	0.051	-0.168	+0.108
2,7	0.030	0.029	0.027	0.025	0.353	0.361	+0.033	-0.352
3,8	0.196	0.194	0.216	0.218	0.005 ^{b)}	0.017	-0.195	-0.014
4,9	0.030	0.029	0.041	0.041	0.147	0.119	+0.065	-0.151
5,10	0.722	0.729	0.712 ⁱ⁾	0.725 ⁱ⁾	0.033	0.068 ⁱ⁾	-0.742	+0.060

a) The meaning of $a_{\text{H}\mu}$ is $a_{\text{H}-\text{C}(x),\text{H}-\text{C}(y)}$, whereas only x and y are usually given.

b) Experimental error ± 0.001 mT, except for $a_{\text{H}5,10}$ (III $^{\ominus}$ and IV $^{\ominus}$) and $a_{\text{H}2,7}$ (III $^{\oplus}$ and IV $^{\oplus}$) where it amounts to ± 0.005 and ± 0.003 mT, respectively.

c) Solvent: DME; counterion: K^{\oplus} ; temp.: 183 K.

d) Solvent: DMF; counterion: $\text{Et}_4\text{N}^{\oplus}$; temp.: 213 K.

e) Solvent: CH_2Cl_2 ; temp.: 273 K.

f) Solvent: CH_2Cl_2 ; temp.: 233 K.

g) Calculated by the *McLachlan* procedure ($\lambda=1.0$) and the *McConnell* equation ($Q=-2.4$ and -2.8 mT for III $^{\oplus}$ and III $^{\ominus}$, respectively).

h) Splitting unresolved; coupling constant estimated from the line-widths by simulation of the ESR. spectrum.

i) Coupling constant of six methyl protons.

Table 2. Proton Coupling Constants, $a_{H\mu}^a$) in mT, for the Radical Ions of Dibenzo[b,f]pentalene (III) and the π -charge Populations, ε_μ , in the Corresponding Diions

μ	III [⊖] $a_{H\mu}^b$)	III ^{2⊖} ε_μ^c)	III [⊕] $a_{H\mu}^b$)	III ^{2⊕} ε_μ^c)
1,6	(-)0.109	-0.065	(+)0.058	+0.141
2,7	(+)0.030	-0.027	(-)0.353	+0.200
3,8	(-)0.196	-0.097	(-)0.005	+0.181
4,9	(+)0.030	-0.033	(-)0.147	+0.177
5,10	(-)0.722	-0.299	(+)0.033	+0.164

a) The meaning of $a_{H\mu}$ is $a_{H-C(x),H-C(y)}$, whereas only x and y are usually given.

b) The signs of $a_{H\mu}$ are those required by theory.

c) The values ε_μ are related to the numbers ρ_i given in [2b] by $\varepsilon_\mu \equiv \varepsilon_i = 1 - \rho_i$.

charge populations ε_μ for III^{2⊕}. These values are subject to an even greater uncertainty than the analogous values ε_μ for III^{2⊖}, since they were evaluated with the use of a correction term σ_μ which allows for the diamagnetic ring currents in dianionic systems [2b]. The assumption that the same term is also appropriate for dications represents undoubtedly a very rough approximation. Nevertheless, in both diions the centres μ accommodating the highest π -charge populations ε_μ are also those bearing the protons with the largest coupling constants $a_{H\mu}$ in the corresponding radical ions.

Comparison with structurally related radical ions. Figure 3 presents the diagrams of the frontier HMO's of pentalene (I) and dibenzo[b,f]pentalene (III). Their inspection reveals some similarity in the shapes of the two LUMO's on the one hand, and of the two HOMO's on the other hand, as far as the centres μ in I and in the pentalene fragment of III are concerned. In particular, the coefficients at the corresponding proton bearing centres μ ($=1,4$ in I and $5,10$ in III) are of like magnitude. The simple MO models thus predict that the π -spin population ρ_μ at

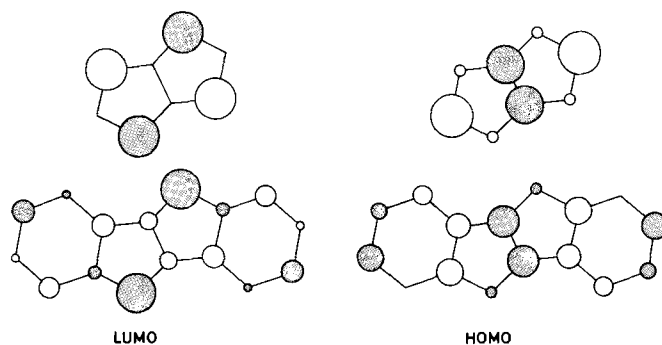
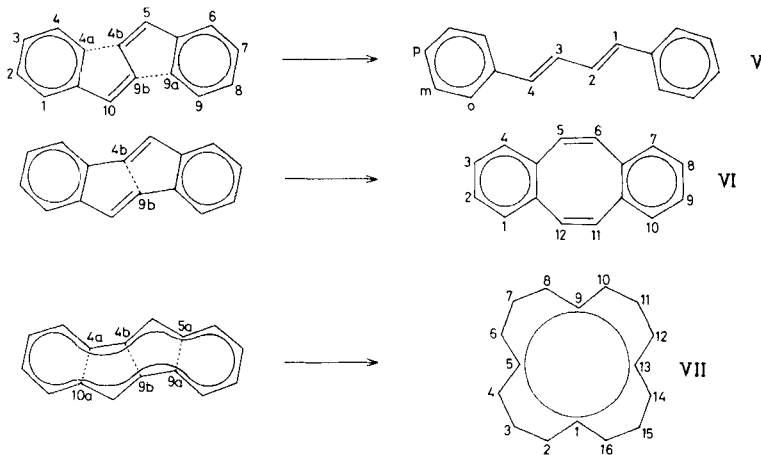


Fig. 3. Lowest antibonding (LUMO's) and highest bonding HMO's (HOMO's) of pentalene (I) and dibenzo[b,f]pentalene (III). The areas of the circles are proportional to the squares of LCAO-coefficients. Blank and shaded areas symbolize opposite signs of these coefficients

3) The compared values $a_{H\mu}$ have been observed under the same experimental conditions: III[⊖] and II[⊖] in DMF at 213 K (counterion Et₄N[⊕]), and III[⊕] and II[⊕] in CH₂Cl₂ at 273 K. Their signs, given in parentheses, are those required by theory.

such centres should be similar in the radical anions I^\ominus and III^\ominus , as well as in the radical cations I^\oplus and III^\oplus . In order to verify this prediction by experiment, the coupling constants $a_{\text{H}5,10}$ for III^\ominus and III^\oplus have to be compared with the analogous values $a_{\text{H}4,6}$ for the radical anion and cation of 1,3,5-tri-*t*-butylpentalene (II) [1], since the radical ions of the highly unstable parent compound I are unknown. Such a comparison, $a_{\text{H}5,10}(\text{III}^\ominus) = (-)0.729$ vs. $a_{\text{H}4,6}(\text{II}^\ominus) = (-)0.661$ mT, and $a_{\text{H}5,10}(\text{III}^\oplus) = (+)0.033$ vs. $a_{\text{H}4,6}(\text{II}^\oplus) = (+)0.040$ mT³, lends support to the predicted similarity in the corresponding π -spin populations ρ_μ .

Apart from representing an annelated non-alternant pentalene, the compound III can be considered as structurally related to 1,4-diphenyl-1,3-butadiene (V), dibenzo[*a, e*]cyclooctene (VI) and [16]annulene (VII). These alternant hydrocarbons, V, VI and VII, are formally derived from III by deleting two peripheral bonds of the five-membered rings (4a-4b, 9a-9b), the central cross-link (4b-9b) and all three cross-links (4a-10a; 4b-9b; 5a-9a), respectively.



The radical anions V^\ominus [11], VI^\ominus [12] [13] and VII^\ominus [14] have been studied by ESR. spectroscopy. Their proton hyperfine data are compared in *Table 3* with the coupling constants $a_{\text{H}\mu}$ for the corresponding positions μ in III^\ominus . (It should be noted that VI^\ominus , in contrast to the neutral compound VI, ought to be planar, or nearly planar [13] [15]. Also VII^\ominus is expected to tend towards planarity [14].)

Clearly, omission of two peripheral bonds 4a-4b and 9a-9b in III^\ominus , to yield V^\ominus , increases the coupling constants of the benzenic protons at the expense of those of the protons in the residual central π -fragment. However, the general pattern of the π -spin distribution is conserved on going from III^\ominus to V^\ominus , as revealed by the unaltered sequence of the analogous values $a_{\text{H}\mu}$.

On the contrary, the data for VI^\ominus and VII^\ominus indicate that removal of the cross-link 4b-9b or of all three cross-links, 4a-10a, 4b-9b and 5a-9a, from III^\ominus , has a much more profound effect on the coupling constants $a_{\text{H}\mu}$. A better insight into the nature of this effect is provided by the calculations of the values $a_{\text{H}\mu}$ as a function of the bond parameter $\beta_{\mu\nu}$ for the cross-links $\mu-\nu$ in question. Such calculations,

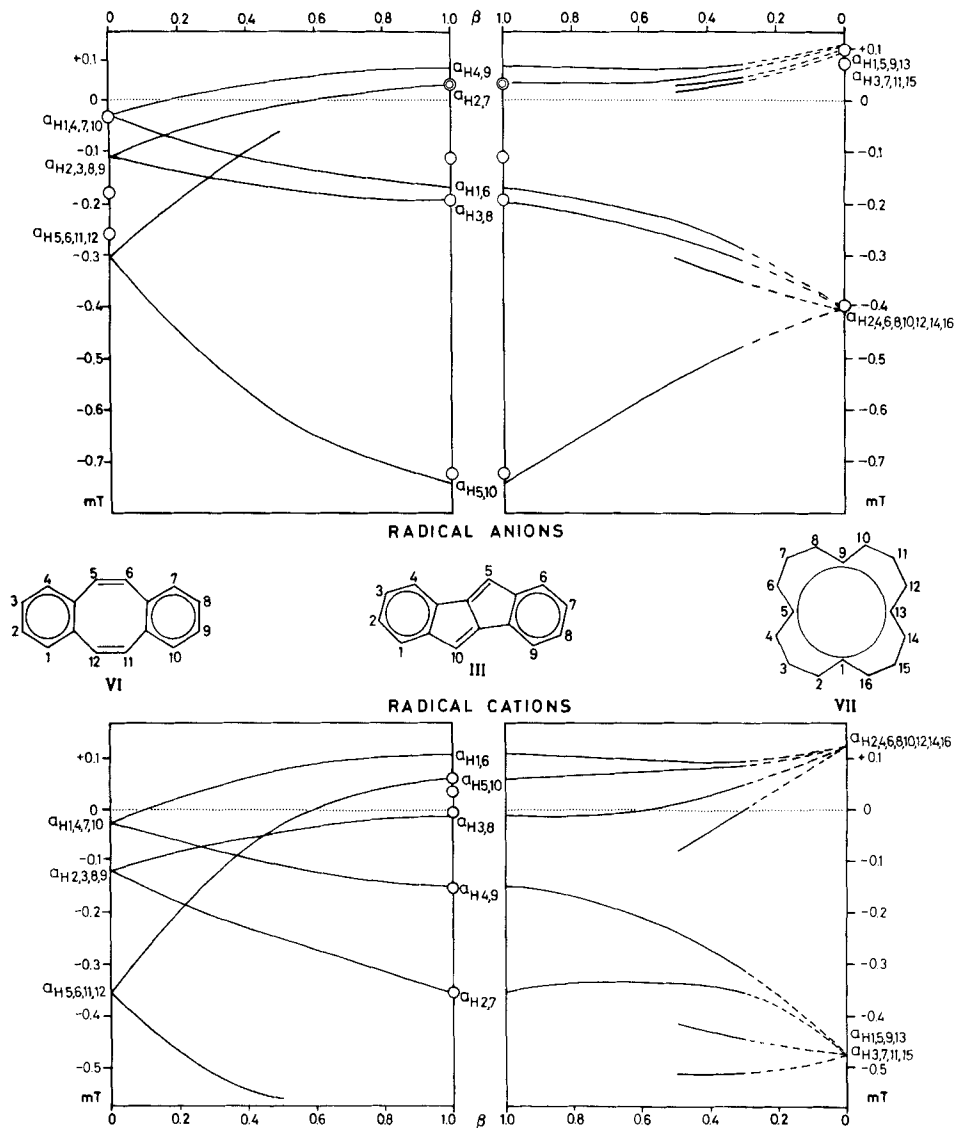


Fig. 4. Proton coupling constants $a_{H\mu}$ calculated for the radical anion (top) and the radical cation (bottom) of dibenzo[b,f]pentalene (III) vs. variable HMO-parameters β_{4b9b} (left) and $\beta_{4a10a} = \beta_{4b9b} = \beta_{5a9a}$ (right). The parts of the curves drawn by dashed lines were obtained by interpolation. The limiting values $a_{H\mu}$ (extreme right) are based on the non-bonding perimeter orbitals, the degeneracy of which is removed in the D_{4h} symmetry. Their sequence in the [16]annulene (VII), a_{1u} above a_{2u} , is consistent with the hyperfine data found for VII^{\ominus} . These data, along with those for III^{\ominus} , III^{\oplus} and VI^{\ominus} , which are also experimentally available (Tables 1 and 3), are represented by circles. They were given signs required by theory.

Table 3. Proton coupling constants, $a_{H\mu}^a$ in mT, for the radical anions of dibenzo[b,f]pentalene (III), 1,4-diphenyl-1,3-butadiene (V), dibenzo[a,e]cyclooctene (VI) and [16]annulene (VII)

III [⊖]		V [⊖]		VI [⊖]		VII [⊖]	
μ	$a_{H\mu}^b$	μ	$a_{H\mu}^b$	μ	$a_{H\mu}^b$	μ	$a_{H\mu}^b$
1,6	(-).0.109	ortho	(-).0.179 ^c	1,7	(-).0.022	4,12	(-).0.396
2,7	(+).0.030	meta	(+).0.063 ^d	2,8	(-).0.184	5,13	(+).0.091 ^e
3,8	(-).0.196	para	(-).0.248	3,9	(-).0.184	6,14	(-).0.396
4,9	(+).0.030	meta	(+).0.063 ^d	4,10	(-).0.022	7,15	(+).0.074 ^e
5,10	(-).0.722	1,4	(-).0.489	6,12	(-).0.260	2,10	(-).0.396

^a) The meaning of $a_{H\mu}$ is $a_{H-C(x),H-C(y)}$, whereas only x and y are usually given.

^b) The signs of $a_{H\mu}$ are those required by theory.

^c) Average of the values (+).0.193 and (+).0.165 mT observed for non-equivalent phenyl ortho-protons.

^d) Average of the values (+).0.076 and (+).0.050 mT observed for non-equivalent phenyl meta-protons.

^e) Assignment uncertain.

carried out by the procedure described above, led to the diagrams displayed in Figure 4 where the coupling constants $a_{H\mu}$ for III[⊖] and, analogously, for III[⊕], are plotted vs. the variables β_{4b9b} (left) and $\beta_{4a10a} = \beta_{4b9b} = \beta_{5a9a}$ (right); for all other bond parameters, their standard value β was retained throughout. These diagrams clearly demonstrate that the striking changes in the coupling constants $a_{H\mu}$ on passing from III[⊖] to VI[⊖] and VII[⊖] are primarily brought about by raising the symmetry from C_{2h} to D_{2h} and D_{4h} , respectively, whereby the π -spin populations undergo a far-reaching redistribution. A direct comparison between the corresponding values $a_{H\mu}$ for the radical ions of related structures, but different symmetries, is therefore not very appropriate.

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