82. Radical Ions of a Bishomobinaphthylene Containing Two 1,6-Methano[10]annulene Moieties: An ESR and ENDOR Study

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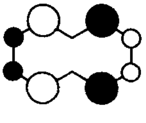
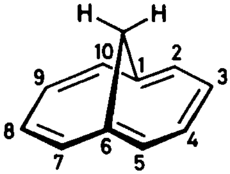
The radical cation and the radical anion of '*syn*'-cyclobuta[1,2-*c*:3,4-*c*']di-1,6-methano[10]annulene ('*syn*'-4a,12a:6a,10a-bishomobinaphthylene; **3**) have been characterized by their hyperfine data. The highly resolved ESR spectrum of $\mathbf{3}^{\ddagger}$ is dominated by a triplet splitting from the outer pair of methano β-protons (H_o). In contrast, the ESR spectrum of $\mathbf{3}^{\bar{\cdot}}$ is poorly resolved with the largest coupling constants arising from perimeter α-protons. The different hyperfine features of $\mathbf{3}^{\ddagger}$ and $\mathbf{3}^{\bar{\cdot}}$ are rationalized by MO models. The SOMO of $\mathbf{3}^{\ddagger}$ $\psi_{SA}(b_1)$, has substantial LCAO coefficients of the same sign at the bridged atoms C(1), C(6), C(11), and C(16), whereas in the SOMO of $\mathbf{3}^{\bar{\cdot}}$, $\psi_{SS}(a_1)$, the four atoms lie in the vertical nodal planes. The large width and the reluctance to saturation of the lines in the ESR spectrum of $\mathbf{3}^{\bar{\cdot}}$ are attributed to the near-degeneracy of the lowest antibonding MO's. Due to their similar nodal properties, the SOMO's of $\mathbf{3}^{\bar{\cdot}}$ and the radical anions of binaphthylene (**4**), 1,6-methano[10]annulene (**1**), and naphthalene (**2**) are interrelated. Moreover, because the cyclic π-systems in **3** and **1** deviate in the same way from planarity, the effect of such distortions on the coupling constants, a_{H_μ}, of the perimeter α-protons in $\mathbf{3}^{\bar{\cdot}}$ and $\mathbf{1}^{\bar{\cdot}}$ should be comparable. Indeed, on going from $\mathbf{4}^{\bar{\cdot}}$ to $\mathbf{3}^{\bar{\cdot}}$, the $|a_{H_\mu}|$ values are reduced exactly by half as much as the corresponding values on passing from $\mathbf{2}^{\bar{\cdot}}$ to $\mathbf{1}^{\bar{\cdot}}$, of which the cyclic π-systems are twice contained in $\mathbf{4}^{\bar{\cdot}}$ and $\mathbf{3}^{\bar{\cdot}}$, respectively.

Introduction. – The synthesis of 1,6-methano[10]annulene (**1**) has been reported nearly 30 years ago [1]. In this bridged ten-membered π-perimeter, which may be regarded as 4a,8a-homonaphthalene, substantial deviations of the π-system from planarity [2] do not seriously affect the cyclic conjugation [3] [4]. Shortly after the synthesis of **1**, the radical anion $\mathbf{1}^{\bar{\cdot}}$ has been characterized by its hyperfine data with the use of ESR spectroscopy [5]. Bridging of the [10]annulene removes the degeneracy of the perimeter LUMO's in such a way that the orbital which is antisymmetric with respect to the vertical mirror plane passing through the bridged atoms C(1) and C(6) has an energy lower than its symmetric counterpart. This is because the latter is destabilized by both the inductive effect of the methano bridging group and the homoconjugative interaction between the $2p_z$-AO's at the formally nonbonded but spatially proximate C(1) and C(6) [5] (see also [6]). Thus, the antisymmetric orbital



becomes the LUMO of **1** and it is the singly occupied MO (SOMO) in $\mathbf{1}^{\cdot-}$. Although this orbital closely resembles the SOMO in the radical anion of naphthalene (**2**), the coupling constants, a_{H_μ}, of the α-protons[1]) at the π-centres in $\mathbf{1}^{\cdot-}$ have their absolute values greatly reduced relative to the corresponding $|a_{H_\mu}|$ values for $\mathbf{2}^{\cdot-}$ [7]. This reduction is considered to be caused by the above-mentioned deviations of the π-perimeter from planarity, because such distortions allow the spin population to delocalize from the π-centres onto the α-protons [5] [8–10]. The contributions to the coupling constants by this spin-transfer mechanism are positive, and they partly compensate the negative a_{H_μ} values due to π-σ spin polarization which is effective for α-protons in planar π-radicals [11].



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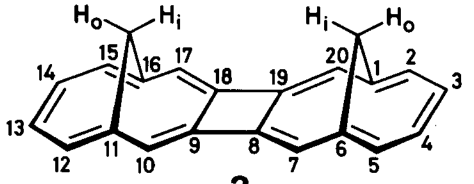

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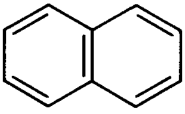

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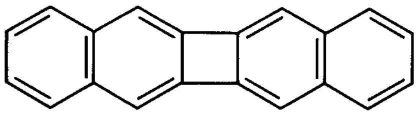

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Recently, '*syn*'-cyclobuta[1,2-*c*:3,4-*c'*]di-1,6-methano[10]annulene ('*syn*'-4a,12a:6a,10a-bishomobinaphthylene; **3**) has been synthesized [12]. Apart from small differences in bond lengths, caused by annelation to the four-membered ring ('*Mills-Nixon* effect' [13]), the X-ray crystallographic structure of the two 1,6-methano[10]annulene moieties in **3** [12] is similar to that of **1** [2]. It was, therefore, of interest to compare the hyperfine data for $\mathbf{3}^{\cdot-}$ with those of $\mathbf{1}^{\cdot-}$ and the radical anion of binaphthylene (**4**) [14]. Of particular concern was the question, whether the observed reductions in the $|a_{H_\mu}|$ values on going from $\mathbf{2}^{\cdot-}$ to $\mathbf{1}^{\cdot-}$ would be reproduced to the same extent, when one passes from $\mathbf{4}^{\cdot-}$ to $\mathbf{3}^{\cdot-}$.

Here, we have characterized the radical anion $\mathbf{3}^{\cdot-}$ by its hyperfine data with the use of ESR spectroscopy. In addition, ESR and ENDOR studies are reported for the corresponding radical cation $\mathbf{3}^{\cdot+}$ which, in contrast to $\mathbf{1}^{\cdot+}$, $\mathbf{2}^{\cdot+}$, and $\mathbf{4}^{\cdot+}$, can be investigated in fluid solution[2]).

Results. – *Radical Cation.* A highly resolved ESR spectrum of $\mathbf{3}^{\cdot+}$ ($g = 2.0028 \pm 0.0001$) was observed upon oxidation of **3** with tris(*p*-bromophenyl)ammoniumyl-$SbCl_6$ in CH_2Cl_2. This spectrum, shown in *Fig. 1*, consists of three well-separated

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[1]) In ESR spectroscopy, protons separated by 0, 1, 2, ... sp^3-hybridized C atoms from the nearest π-centre, are denoted α, β, γ...

[2]) Attempts to generate $\mathbf{1}^{\cdot+}$ from **1** with $AlCl_3$ or tris(*p*-bromophenyl)ammoniumyl-$SbCl_6$ in CH_2Cl_2 failed thus far [15]. Oxidation of **2** by $SbCl_5$ in CH_2Cl_2 yielded a dimeric radical cation $\mathbf{2}_2^{\cdot+}$ [16] [17]. ESR and ENDOR spectra of monomeric $\mathbf{2}^{\cdot+}$ were only observed upon γ-irradiation of **2** in a $CFCl_3$ matrix [18]. An unsuccessful attempt to produce $\mathbf{4}^{\cdot+}$ from **4** in conc. H_2SO_4 was mentioned in the early publication on $\mathbf{4}^{\cdot-}$ [14]. Later on, it was reported [19] that the 5,6,11,12-tetramethyl derivative of **4** fails to yield its radical cation with $AlCl_3$ in CH_2Cl_2, although substitution by alkyl groups in these four positions is expected to markedly lower the oxidation potential of **4**.

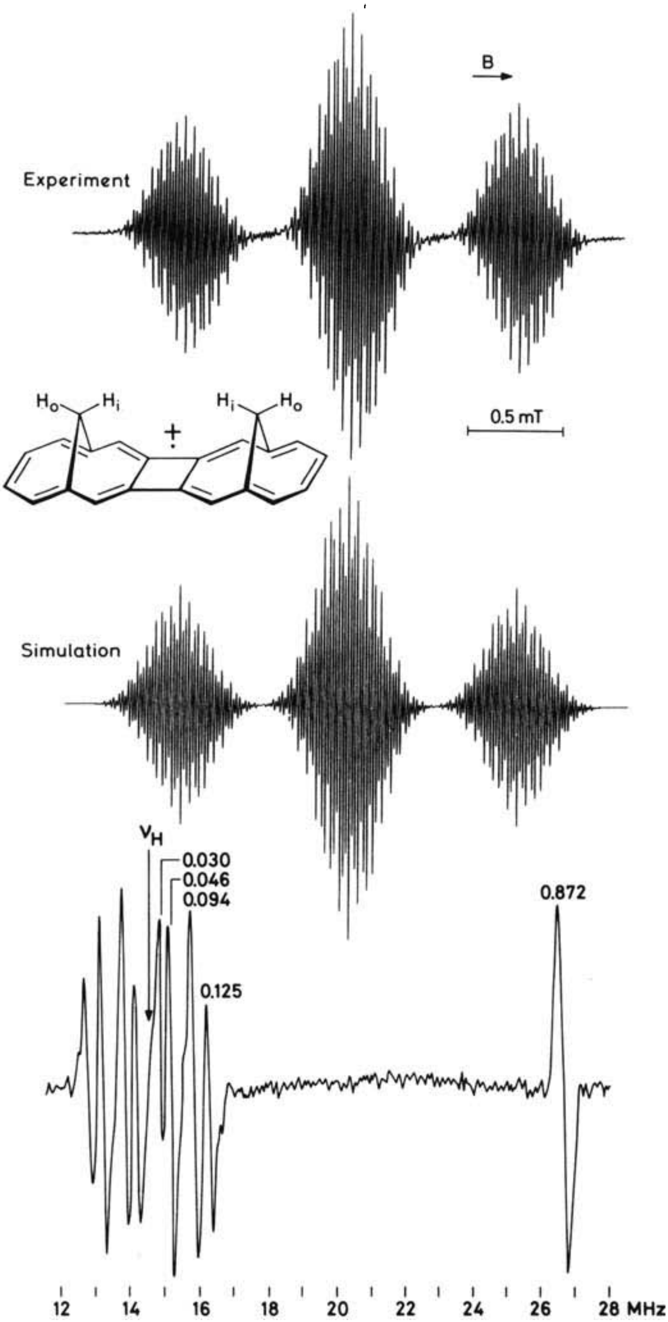

Fig. 1. *ESR and proton-ENDOR spectra of* $3^{+\cdot}$. Solvent: CH_2Cl_2; counterion: $SbCl_6^-$; temp.: 203 K. The simulation of the ESR spectrum (*top*) made use of the coupling constants given in the text and *Fig. 4*; line-shape: *Lorentz*ian; line-width: 0.010 mT. The numbers above the ENDOR signals (*bottom*) are the coupling constants [mT] associated with these signals.

groups of lines, due to a hyperfine interaction with two protons having a coupling constant of 0.872 ± 0.003 mT. The splittings within each group stem from a further pair of protons with 0.125 ± 0.001 mT and three sets of four protons with 0.094 ± 0.001, 0.046 ± 0.001, and 0.030 ± 0.001 mT. All coupling constants were also observed by the ENDOR technique, and the analysis was confirmed by computer simulation of the ESR spectrum (*Fig. 1*). A general-TRIPLE-resonance experiment indicated that the sign of 0.094 mT is opposite to that of the four remaining values.

Radical Anion. Reaction of **3** with K in 1,2-dimethoxyethane (DME), THF, or 2-methyl-THF (MTHF) yielded $\mathbf{3}^{\cdot-}$, of which the ESR spectrum ($g = 2.0028 \pm 0.0001$) is reproduced in *Fig. 2*. The same spectrum was observed upon electrolytic reduction of **3** in DME (helical Au-Hg cathode, Pt anode in the cell axis, Bu_4NPF_6 as the supporting salt [20]). In sharp contrast to $\mathbf{3}^{\cdot+}$, the spectrum of $\mathbf{3}^{\cdot-}$ exhibited a poor resolution which could not be improved by variation of concentration (10^{-3} to 10^{-5} mol/dm^3), temperature (193 to 298 K), solvent (DME, THF, MTHF), and counterion (K^+, Bu_4N^+). Nor it was possible to saturate the broad ESR lines, so that application of the ENDOR technique had to be renounced. Nevertheless, careful and repeated simulations of the ESR spectrum, combined with resolution enhancement [21], revealed three coupling constants, each for a set of four protons: 0.277 ± 0.010, 0.097 ± 0.005, and 0.058 ± 0.003 mT. A further unresolved splitting of 0.005 ± 0.002 mT by four protons was estimated from the line-width.

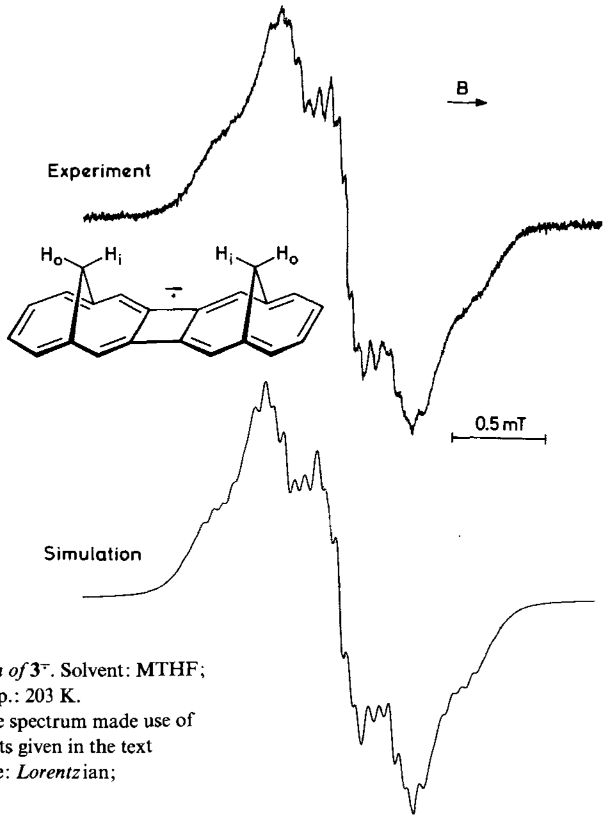

Fig. 2. *ESR Spectrum of* $\mathbf{3}^{\cdot-}$. Solvent: MTHF; counterion: K^+; temp.: 203 K.
The simulation of the spectrum made use of the coupling constants given in the text and *Fig. 4*; line-shape: *Lorentz*ian; line-width: 0.10 mT.

Discussion. – *MO Models. Fig. 3* shows diagrammatically the two highest bonding orbitals, ψ_{AA} and ψ_{SA}, and the two lowest antibonding ones, ψ_{AS} and ψ_{SS}, for the *Hückel* model of a cyclobutadi[10]annulene. The subscripts S and A mean symmetric and antisymmetric, respectively, with regard to the vertical mirror planes xz (1. letter) and yz (2. letter). The parameter $\beta_{8\text{-}9} = \beta_{18\text{-}19} = k\beta$ with $k = 0.85$ is used for the 'essential single bonds' C(8)–C(9) and C(18)–C(19) linking the [10]annulene moieties, because studies on the radical ions of benzo[*b*]biphenylene [19] have indicated that a value in this range of k should be appropriate for such bonds in the four-membered ring. Homoconjugation, due to the overlapping of the $2p_z$-AO's at the formally nonbonded but spatially proximate atoms C(1), C(6) and C(11), C(16), is taken into account by introducing a parameter $\beta_{1\text{-}6} = \beta_{11\text{-}16} = k'\beta$ with $k' = 0.4$, while inductive perturbation of these atoms by the bridging methano groups is allowed for by setting $\alpha_1 = \alpha_6 = \alpha_{11} = \alpha_{16} = \alpha + h\beta$ with $h = -0.3$.

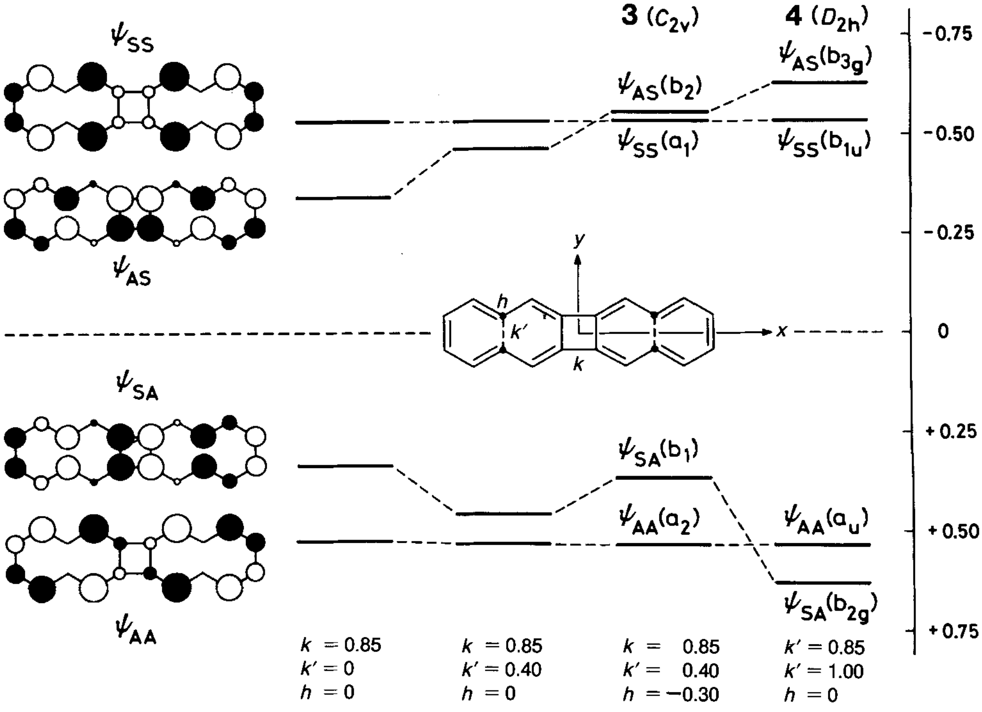

Fig. 3. *Diagrams of the two highest bonding and the two lowest antibonding MO's for the* Hückel *model of a cyclobutadi[10]annulene. Effect on the MO levels due to linking C(1) with C(6) and C(11) with C(16) by CH_2 groups* (**3**) *or directly by bonds* (**4**). The energy scale is in units of β.

To the first-order approximation, both modifications ($k' = 0.4$ and $h = -0.3$) do not affect ψ_{AA} and ψ_{SS}, because the involved atoms, C(1), C(6), C(11), and C(16), lie in the vertical nodal planes of the two MO's. On the other hand, ψ_{SA} and ψ_{AS}, which exhibit large coefficients at the four bridged C-atoms, undergo marked energy shifts by these modifications. Whereas for ψ_{SA} the homoconjugative ($k' = 0.4$) and the inductive ($h = -0.3$) perturbations work in opposite directions, so that their effects on the MO energy partially cancel, they enhance each other in the case of ψ_{AS}. Therefore, the energetic sequence of the bonding MO's, ψ_{SA} above ψ_{AA}, remains unchanged, but, in the antibonding range, ψ_{AS} is to such an extent destabilized that it slightly exceeds ψ_{SS} in energy (*Fig. 3*). This prediction of the *Hückel* model for **3** is confirmed by an INDO calculation [22][3]) which yields the following MO energies in eV: $-9.8(\psi_{AA})$, $-7.6(\psi_{SA})$, $+1.4(\psi_{SS})$, and $+1.5(\psi_{AS})$.

By setting $\beta_{1-6} = \beta_{11-16} = \beta$, *i.e.*, $k' = 1.0$ ($k = 0.85$; $h = 0$) for additional C(1)–C(6) and C(11)–C(16) π-bonds, the same model can be used to derive the frontier MO's of binaphthylene (**4**). Again, due to their nodal properties, the energies of ψ_{AA} and ψ_{SS} remain unchanged to the first-order approximation, whereas ψ_{SA} and ψ_{AS} with the large coefficients at C(1), C(6), C(11), and C(16) are strongly shifted. Thereby, ψ_{SA} is clearly stabilized, and ψ_{AS} is to the same extent destabilized relative to ψ_{AA} and ψ_{SS}, respectively (*Fig. 3*). As a result, ψ_{AA} becomes the HOMO of **4**, correlating with the next highest bonding MO of **3**, while the LUMO of **4**, like that of **3**, is represented by ψ_{SS}.

Comparison with Experiment. Considering the different shapes of ψ_{SA} and ψ_{SS}, the coupling constants of the protons in $\mathbf{3}^{+\cdot}$ and $\mathbf{3}^{-\cdot}$ are expected to differ strongly, as it has, indeed, been observed. Moreover, the predicted accidental near-degeneracy of ψ_{SS} and ψ_{AS} nicely tallies with the large width and reluctance to saturation of the lines in the ESR spectrum of $\mathbf{3}^{-\cdot}$, because these features are symptomatic of a degenerate or nearly degenerate ground state subject to a dynamic *Jahn-Teller* effect [24] [25] (for analogous examples, see [26] [27]). Contrary to $\mathbf{3}^{+\cdot}$ and $\mathbf{3}^{-\cdot}$, the radical ions of binaphthylene, $\mathbf{4}^{+\cdot}$ and $\mathbf{4}^{-\cdot}$, should give rise to similar ESR spectra, in accord with the pairing properties of the HOMO and LUMO in alternant hydrocarbons [28]. Unfortunately, this prediction could not be verified by experiment because of the failure to observe the ESR spectrum of $\mathbf{4}^{+\cdot}$[2]). Nevertheless, the finding that **4** is harder to oxidize than **3** is in agreement with the MO model which places the HOMO (ψ_{AA}) of **4** well below that of **3** (ψ_{SA}). Likewise, the easy reduction of both compounds to their radical anions $\mathbf{3}^{-\cdot}$ and $\mathbf{4}^{-\cdot}$, having comparable hyperfine data, is consistent with their SOMO's being traced back to the same orbital (ψ_{SS}).

The single occupancy of ψ_{SA} in $\mathbf{3}^{+\cdot}$ should manifest itself by the hyperfine interaction with the β-protons[1]) in the methano bridging groups, each of which is simultaneously linked to two π-centres μ, C(1) and C(6), or C(11) and C(16), bearing substantial LCAO coefficients of the same sign. Such a structural feature is known to give rise to large β-proton coupling constants [29] (for related radical ions of methano-bridged annulenes, see also [6] [30]). In fact, the dominant hyperfine splitting of 0.872 mT observed for $\mathbf{3}^{+\cdot}$ stems from one pair of methano β-protons, while the second pair of such protons is responsible for the next largest, albeit considerably smaller, coupling constant of 0.125 mT. Assignments of 0.872 mT to the outer (H_o) and 0.125 mT to the inner (H_i) protons, are indicated by the INDO calculations[3]) which predict that the former should have a coupling constant by one order of magnitude larger than the latter. Use of the two observed values in the $\cos^2\theta$ relation for β-proton coupling constants [29] [31], where θ is

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[3]) The calculations are based on MM2 [23] geometry which mimics the X-ray crystallographic structure of **3** [12]. The X-ray data have not directly been used, because they imply a torsion along the x-axis and are, thus, incompatible with the C_{2v} symmetry reflected by the ESR spectra of $\mathbf{3}^{+\cdot}$ and $\mathbf{3}^{-\cdot}$. As this symmetry is also indicated by the ^{1}H- and ^{13}C-NMR spectra of **3** in solution [12], the distortion found in the crystalline state must be caused by intermolecular packing forces.

the dihedral angle between the $2p_z$-axis at a bridged centre μ and the C–H_β bond, yields $\theta_o = 45.4$ and $\theta_i = 74.6°$ for C–H_o and C–H_i, respectively. As both 0.872 and 0.125 mT are certainly positive, it follows from the general-TRIPLE experiment that 0.046 and 0.030 mT must also be positive, while 0.094 mT should have a negative sign. Assignments of -0.094 mT to the set of four α-protons in the 3,4,13,14-positions and of $+0.046$ and $+0.030$ mT to such sets in the 7,10,17,20- and 2,5,12,15-positions, respectively, are based on the squared LCAO coefficients for ψ_{SA}, corrected by the *McLachlan* procedure [32], and they are compatible with the results of the INDO calculations.

These assignments of coupling constants for $\mathbf{3}^{+}$, as well as those for $\mathbf{3}^{\overline{\cdot}}$ (to be discussed below) are indicated in *Fig. 4* which also presents the reported hyperfine data for the radical anions of 1,6-methano[10]annulene (**1**) [5] [8], naphthalene (**2**) [7], and binaphthylene (**4**) [14]. Theory predicts a negative sign for all coupling constants of protons in $\mathbf{1}^{\overline{\cdot}}$–$\mathbf{4}^{\overline{\cdot}}$; this prediction agrees with the general-TRIPLE-resonance spectra of $\mathbf{1}^{\overline{\cdot}}$ and $\mathbf{2}^{\overline{\cdot}}$ [15] which require that all values have the same sign.

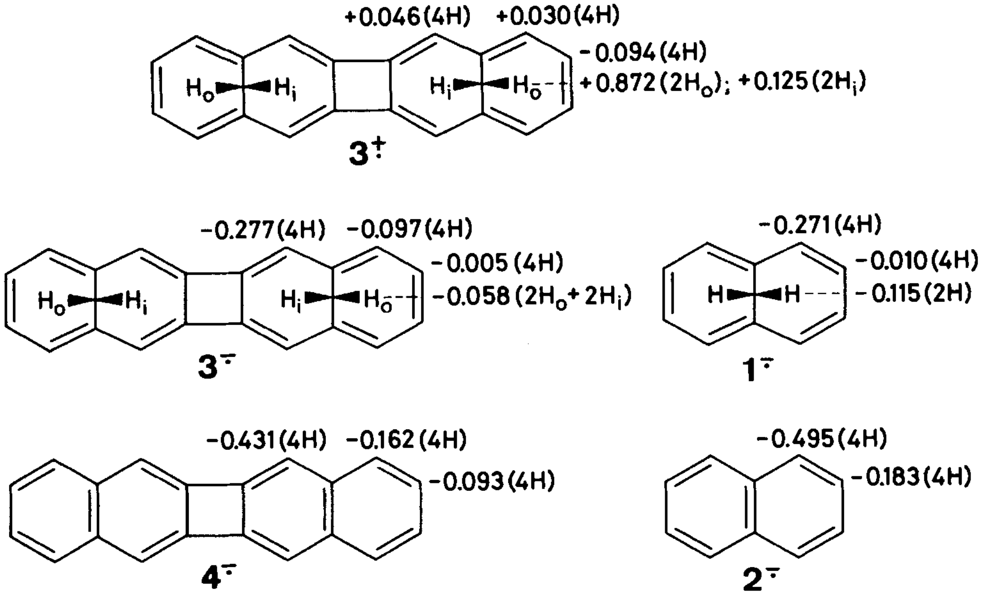

Fig. 4. *Proton-coupling constants* [mT] *for* $\mathbf{3}^{+}$ *and* $\mathbf{1}^{\overline{\cdot}}$–$\mathbf{4}^{\overline{\cdot}}$

The hyperfine data for $\mathbf{3}^{\overline{\cdot}}$ are fully consistent with the single occupancy of ψ_{SS}. Assignments of the coupling constants to sets of protons can, thus, be based on the squared LCAO coefficients for this orbital, corrected by the *McLachlan* procedure, and on the results of the INDO calculations. However, as the agreement between the experimental and theoretical values is only qualitative, some additional evidence in favor of these assignments appears to be desirable. In this respect, it is important to note that, beyond representing the SOMO of $\mathbf{3}^{\overline{\cdot}}$ and $\mathbf{4}^{\overline{\cdot}}$, ψ_{SS} can be regarded as a bonding combination of two such MO's in **1**$^{\cdot-}$ and **2**$^{\cdot-}$ (see *Introduction*). As is evident from *Fig. 4* and the *Table*, the assignments made for **3**$^{\cdot-}$ connect the hyperfine data of the four radical anions in such a way that the changes in the α-proton coupling constants, a_{H_μ}, on going from **4**$^{\cdot-}$ to **3**$^{\cdot-}$ are almost exactly half as large as those on passing from **2**$^{\cdot-}$ to **1**$^{\cdot-}$. Apart from serving for a support of the assignments in question, this impressive coincidence allows the following conclusion to be drawn: *Similar deviations of the π-system from planarity have a similar effect on the α-proton-coupling constants provided that the SOMO's of the radicals are interrelated.*

Table. *Comparison of the α-Proton-Coupling Constants,* a_{H_μ} [mT], *for* **1**$^{\cdot-}$–**4**$^{\cdot-}$. The relevant values are given in italics (last column).

Position μ[a])	$a_{H_\mu}(\mathbf{3}^{\cdot-})$	$a_{H_\mu}(\mathbf{4}^{\cdot-})$	$[a_{H_\mu}(\mathbf{3}^{\cdot-}) - a_{H_\mu}(\mathbf{4}^{\cdot-})]$	
7, 10, 17, 20	–0.277	–0.431	+0.154	*+0.110*[b])
2, 5, 12, 15	–0.097	–0.162	+0.065	
3, 4, 13, 14	–0.005	–0.093	+0.088	*+0.088*
	$a_{H_\mu}(\mathbf{1}^{\cdot-})$	$a_{H_\mu}(\mathbf{2}^{\cdot-})$	$[a_{H_\mu}(\mathbf{1}^{\cdot-}) - a_{H_\mu}(\mathbf{2}^{\cdot-})]$	
2, 5, 7, 10	–0.271	–0.495	+0.224	2 × (*+0.112*)
3, 4, 8, 9	–0.010	–0.183	+0.173	2 × (*+0.087*)

[a]) For clarity, the numbering of the positions in **3** and **4** has been retained for **1** and **2**, respectively.

[b]) Average value.

Assignment of –0.058 mT to all four methano β-protons in **3**$^{\cdot-}$, which have no counterparts in **4**$^{\cdot-}$, seems straightforward in view of the double as large value observed for such protons in **1**$^{\cdot-}$. This assignment is again supported by the INDO calculations which yield almost equal (negative) coupling constants for both H_o and H_i, in contrast to the strongly differing corresponding (positive) values for **3**$^{\cdot+}$. At first sight, such a result is difficult to understand, because the same geometry has been used in the calculations for both **3**$^{\cdot+}$ and **3**$^{\cdot-}$. A more detailed analysis of the INDO results, however, reveals that the effective equalization of the coupling constants for H_o and H_i in **3**$^{\cdot-}$ is due to contributions from spin polarization of the doubly occupied MO's. Such a contribution is usually neglected for β-proton coupling constants which arise mainly by π-σ spin delocalization from the π-orbital onto the β-protons (hyperconjugation), and which depend essentially on the conformation of the C–H_β bond as expressed by their dependence on $\cos^2\theta$ [31].

Experimental. – The synthesis of **3** has been described in [12]. The ESR spectra were taken on a *Varian-E9* instrument, while a *Bruker-ESP-300* system served for ENDOR and TRIPLE-resonance studies.

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