Effect of Nonplanarity in Bridged [14]Annulenes on the Electron Spin Resonance Spectra of Their Radical Anions

F. Gerson,*[1a] K. Müllen,[1a] and E. Vogel[1b]

Contribution from Physikalisch-Chemisches Institut der Universität Basel, Basel, Switzerland, and Chemisches Institut der Universität Köln, Köln, Germany.
Received August 2, 1971

Abstract: Esr spectra are reported for the radical anions of eight bridged [14]annulenes **1**–**8** (Figure 1). The coupling constants of the ring protons in $\mathbf{1}^-$–$\mathbf{8}^-$ exhibit marked differences which can be rationalized in terms of two major effects: nonplanarity of the 14-membered perimeter and the (electronic) substituent effect of the bridging groups. Under the reasonable assumption that the geometry remains practically unchanged on conversion of one of the bridged [14]annulenes to its radical anion, the sequence $\mathbf{8} < \mathbf{5} < \mathbf{4} \approx \mathbf{3} \approx \mathbf{2} \approx \mathbf{1} < \mathbf{6} \lesssim \mathbf{7}$ is obtained for increasing planarity of the individual compounds. It is noteworthy that, although this sequence meets the requirements of molecular models, it cannot be readily deduced from the electronic and proton resonance spectra; the latter allow a clear-cut differentiation only between the "olefinic" anti-bridged [14]annulene **8** and its "aromatic" syn-bridged counterparts **1**–**7** as a whole. The differences in the coupling constants of the methine bridge protons in $\mathbf{5}^-$, $\mathbf{4}^-$, and $\mathbf{6}^-$ can also be interpreted by changes in geometry. In the case of $\mathbf{8}^-$, the esr data are consistent with a double bond localization previously postulated for the parent neutral compound.

In the last few years, the bridged [14]annulenes **1**–**8** (see the formulas in Figure 1 and Table I) have been synthesized by Vogel and coworkers.[2,3] Sufficient planarity of the 14-membered, anthracene-like perimeter is the prerequisite for a substantial cyclic π delocalization and an "aromatic" character of the compounds **1**–**8**. According to molecular models, the perimeter in the syn-bridged [14]annulenes **1**–**7** should exhibit the required planarity, and, in fact, the spectroscopic and chemical behavior of these compounds fully justifies their characterization as aromatic. On the other hand, molecular models demonstrate that the $2p\pi$ orbital axes at the bridgehead carbon atoms in the *anti*-bismethano[14]annulene **8** are considerably twisted out of alignment. Such a twisting impedes the cyclic π delocalization and accounts for the olefinic character as reflected by the physicochemical properties of **8**.[3]

The general characterization of the syn-bridged [14]annulenes **1**–**7** as aromatic does not reveal, however, the finer differences in geometry among the individual compounds. Clearly, the degree of planarity achieved by the 14-membered perimeter in **1**–**7** must depend on the nature of the bridging group. Although a sequence $\mathbf{5} < \mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4} < \mathbf{6}, \mathbf{7}$ of increasing planarity is predicted by molecular models, experimental evidence in its favor has been scanty so far. X-Ray data are available only for **1**[4] and **4**;[5] they confirm the almost identical geometry of the perimeter in the two compounds. As for the electronic and proton resonance spectra, the differences observed in the syn series are not large enough to serve as a clear-cut test for changes in geometry.[2] This relative lack of sensitivity is not surprising, since the nonplanarity of the perimeter in the syn-bridged [14]annulenes **1**–**7** implies twisting angles φ of less than 30° for two consecutive $2p\pi$ orbitals.[4,5] Assuming that the resonance integral (β) between the two orbitals depends on cos φ, the resulting decrease does not exceed 15%, and the cyclic π delocalization remains practically unaffected. Only for essentially larger φ values, as seem to occur in the anti-bridged [14]annulene **8**, is there a substantial reduction in the resonance integrals, and the cyclic π delocalization is effectively impaired.

In contrast to their relatively weak influence on the electronic and proton resonance spectra of **1**–**7**, moderate deviations of the perimeter from planarity should have a pronounced effect on the esr spectra of the corresponding radical anions $\mathbf{1}^-$–$\mathbf{7}^-$. For reasons to be considered in the Discussion, the coupling constants of the ring protons in $\mathbf{1}^-$–$\mathbf{7}^-$ should be very sensitive to such deviations, as are the analogous values for related radical anions.[6,7] We thus expect that these coupling constants will indicate the extent to which the cyclic π system in $\mathbf{1}^-$–$\mathbf{7}^-$ achieves a coplanar arrangement. Moreover, since the geometry of the perimeter in **1**–**7** is fixed by the bridging groups, it cannot be significantly altered by the uptake of an additional electron. We thus also expect that information inferred from the esr spectra of the radical anions will be characteristic of the parent neutral compounds as well.

The results of esr studies reported in the present paper for $\mathbf{1}^-$–$\mathbf{7}^-$ meet these expectations, being in good agreement with the sequence suggested by molecular models. We therefore wish to propose that *the coupling constants of the ring protons in the radical anions* $\mathbf{1}^-$–$\mathbf{7}^-$ *are a criterion for the planarity of the perimeter in corresponding neutral compounds* **1**–**7**. This criterion also applies to the radical anion $\mathbf{8}^-$, the esr data of which reflect the high degree of nonplanarity established for the parent anti-bridged [14]annulene **8**.

---

(1) (a) Universität Basel; (b) Universität Köln.

(2) E. Vogel, M. Biskup, A. Vogel, and H. Günther, *Angew. Chem.*, **78**, 755 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 734 (1966); E. Vogel, A. Vogel, H.-K. Kübbeler, and W. Sturm, *Angew. Chem.*, **82**, 512 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 514 (1970); E. Vogel, W. Sturm, and H. D. Cremer, *Angew. Chem.*, **82**, 513 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 516 (1970); E. Vogel, U. Haberland, and J. Ick, *Angew. Chem.*, **82**, 514 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 517 (1970); E. Vogel and H. Reel, *J. Amer. Chem. Soc.*, to be published.

(3) E. Vogel, U. Haberland, and H. Günther, *Angew. Chem.*, **82**, 510 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 513 (1970).

(4) P. Ganis and J. D. Dunitz, *Helv. Chim. Acta*, **50**, 2369 (1967).

(5) G. Casolone, A. Gavezzotti, A. Mugnoli, and M. Simonetta, *Angew. Chem.*, **82**, 516 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 519 (1970).

(6) F. Gerson, E. Heilbronner, W. A. Böll, and E. Vogel, *Helv. Chim. Acta*, **48**, 1494 (1965).

(7) F. Gerson, J. Heinzer, and E. Vogel, *ibid.*, **53**, 95 (1970).

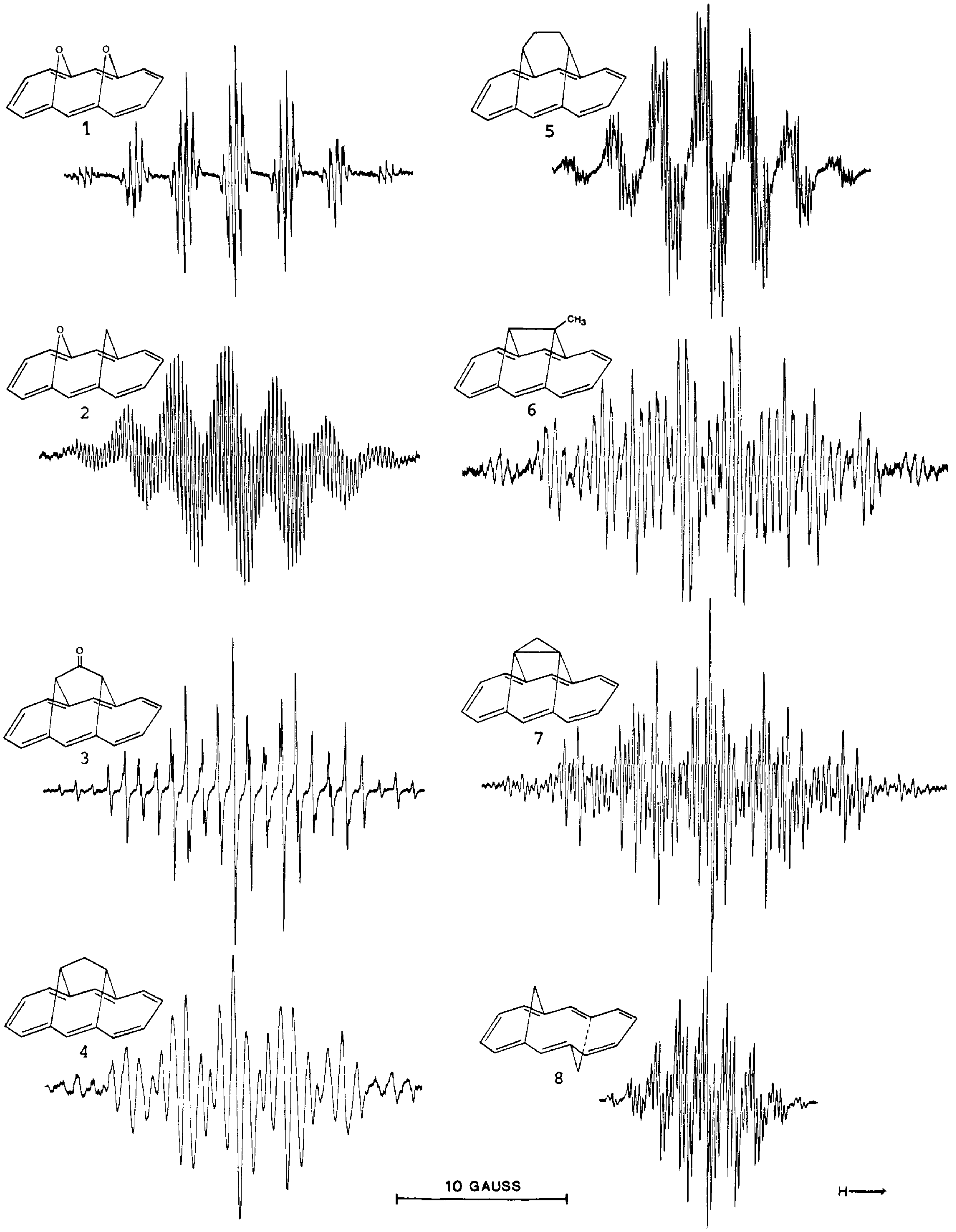


Figure 1. Esr spectra of radical anions 1^-–8^-: solvent, DMF; gegenion, $(C_2H_5)_4N^+$; temperature, +20° for 1^- and −60° for 2^-–8^-.

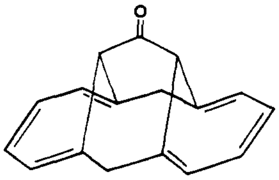
Results

Preparation of the Radical Anions. Although the radical anions 1^-–8^- can be prepared from the corresponding bridged [14]annulenes by both electrolytical reduction and reaction with an alkali metal, the former method is preferable to the latter for two reasons. (a)

Practically no dianions $\mathbf{1}^{2-}$–$\mathbf{8}^{2-}$ are formed on electrolysis when the applied voltage remains sufficiently low.[8] On the other hand, reactions of **1–8** with alkali metals always yield appreciable quantities of dianions. (b) Use of electrolysis in relatively polar solvents prevents the radical anions from associating closely with their gegenions. Such an association is frequently observed for radical anions prepared by reaction with alkali metals in nonpolar solvents.

Formation of the dianion and association with the gegenion are known to affect the esr spectrum of the radical anion by impairing the resolution and complicating the hyperfine structure.[9] To avoid these unwanted effects, all the esr studies described in the present paper have been carried out on electrolytically reduced compounds. *N*,*N*-Dimethylformamide (DMF) and tetraethylammonium perchlorate were used as solvent and supporting salt, respectively. At −60° all the radical anions exhibited sufficient stability for convenient esr investigations. As the temperature was raised, a slow decrease of radical concentrations occurred, such a decrease being markedly more rapid for the anti-bridged anion $\mathbf{8}^{-}$ than for its syn-bridged counterparts $\mathbf{1}^{-}$–$\mathbf{7}^{-}$. The stability of the radical anions thus parallels that of the parent neutral compounds **1–8**.[2,3]

It is noteworthy that the radical anion $\mathbf{3}^{-}$ can be also obtained from the dihydro derivative **9**.[2]



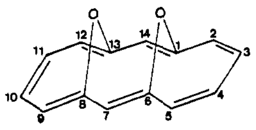
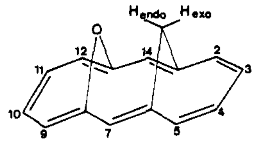
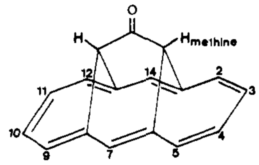
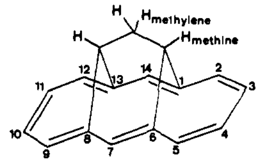
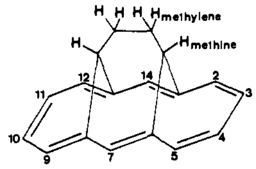
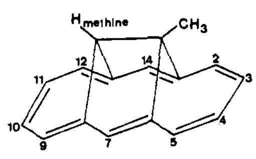
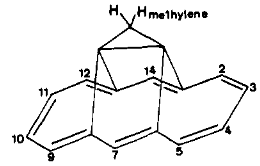
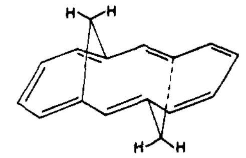
9

Electrolysis of **9** yielded first the short-lived radical anion $\mathbf{9}^{-}$, which gives rise to a complex esr spectrum of low intensity. After a few minutes this spectrum was replaced by that of $\mathbf{3}^{-}$ (Figure 1). A spontaneous release of two hydrogen atoms thus takes place, the driving force being the gain in cyclic π-delocalization energy on passing from $\mathbf{9}^{-}$ to $\mathbf{3}^{-}$.

Esr Spectra. Figure 1 shows the spectra of the radical anions $\mathbf{1}^{-}$–$\mathbf{8}^{-}$; that of $\mathbf{1}^{-}$ has been reproduced from a previous paper[10] for completeness. The spectra of $\mathbf{2}^{-}$–$\mathbf{8}^{-}$ were taken at −60°, that of $\mathbf{1}^{-}$ at +20°. Variation of temperature has only a slight effect on the hyperfine structures of the radical anions $\mathbf{1}^{-}$–$\mathbf{8}^{-}$, a behavior contrasting with the marked temperature dependence found for the coupling constants of the protons in the radical anions of 1,6-bridged [10]annulenes.[11,12]

Analysis of the hyperfine structures of $\mathbf{1}^{-}$–$\mathbf{8}^{-}$ yields the proton coupling constants listed in Table I. These values result from repeated computer simulation in which the coupling constants and/or line widths were systematically varied until the experimental and theo-

Table I. Coupling Constants of Protons (and of Some ^{13}C Nuclei) in the Radical Anions of Bridged [14]Annulenes **1–8**

Radical anion of	Coupling constants, G^{a}	Assignment
 **1**	2.95^{b} (four ^{1}H)	2, 5, 9, 12
	0.37^{b} (four ^{1}H)	3, 4, 10, 11
	2.88^{b} (two ^{1}H)	7, 14
	5.7 ± 0.1^{b} (four ^{13}C)	1, 6, 8, 13
	4.9 ± 0.1^{b} (four ^{13}C)	2, 5, 9, 12
	7.3 ± 0.1^{b} (two ^{13}C)	7, 14
 **2**	2.31 (two ^{1}H)	2, 5
	0.24 (two ^{1}H)	3, 4
	3.26 (two ^{1}H)	7, 14
	3.02 (two ^{1}H)	9, 12
	0.48 (two ^{1}H)	10, 11
	0.93 (one ^{1}H)	Exo
	0.48 (one ^{1}H)	Endo
 **3**	2.77 (four ^{1}H)	2, 5, 9, 12
	<0.05^{c} (four ^{1}H)	3, 4, 10, 11
	3.60 (two ^{1}H)	7, 14
	0.92 (two ^{1}H)	Methine
 **4**	2.78 (four ^{1}H)	2, 5, 9, 12
	<0.05^{c} (four ^{1}H)	3, 4, 10, 11
	3.44 (two ^{1}H)	7, 14
	0.88 (two ^{1}H)	Methine
	0.12^{d} (two ^{1}H)	Methylene
	5.4 ± 0.1 (four ^{13}C)	1, 6, 8, 13
	5.0 ± 0.1 (four ^{13}C)	2, 5, 9, 12
	7.4 ± 0.1 (two ^{13}C)	7, 14
 **5**	2.42 (four ^{1}H)	2, 5, 9, 12
	<0.05^{c} (four ^{1}H)	3, 4, 10, 11
	2.77 (two ^{1}H)	7, 14
	0.47 (two ^{1}H)	Methine
	0.18 (four ^{1}H)	Methylene
 **6**	3.20 (two ^{1}H)	2, 5 or 9, 12
	0.58 (two ^{1}H)	3, 4 or 10, 11
	4.39 (two ^{1}H)	7, 14
	3.09 (two ^{1}H)	9, 12 or 2, 5
	0.43 (two ^{1}H)	10, 11 or 3, 4
	2.65 (one ^{1}H)	Methine
	<0.08^{c} (three ^{1}H)	Methyl
 **7**	3.16 (four ^{1}H)	2, 5, 9, 12
	0.81 (four ^{1}H)	3, 4, 10, 11
	4.52 (two ^{1}H)	7, 14
	0.28 (two ^{1}H)	Methylene
 **8**	1.64 (two ^{1}H)	*e*
	1.59 (two ^{1}H)	*e*
	1.19 (two ^{1}H)	*e*
	1.14 (two ^{1}H)	*e*
	0.20 (two ^{1}H)	*e*

[a] Number of nuclei responsible for the coupling constant are given in parentheses. [b] Values taken from ref 10. [c] Splitting unresolved. [d] Splitting partially resolved. [e] Coupling constants presumably due to ring protons (see Discussion).

---

[8] The half-wave polarographic potentials, which have been measured for the first and second one-electron reduction steps of the compounds **1–5**, are separated by 0.6–0.7 V: K. Müllen, Thesis, Universität Basel, 1971.

[9] See, *e.g.*, F. Gerson, "High Resolution ESR Spectroscopy," Verlag Chemie, Weinheim/Bergstr., Germany, and Wiley, New York, N. Y., 1970, Chapters 1.3 and A.2.2.

[10] F. Gerson, J. Heinzer, and E. Vogel, *Helv. Chim. Acta*, **53**, 103 (1970).

[11] F. Gerson and J. H. Hammons, "Nonbenzenoid Aromatics," Vol. II, J. P. Snyder, Ed., Academic Press, New York, N. Y., 1970, p 81.

[12] F. Gerson, K. Müllen, and E. Vogel, *Helv. Chim. Acta*, **54**, 2731 (1971).

retical spectra agreed in every essential feature.[13] The final numbers given in Table I for proton hyperfine splittings are thus likely to be exact within ±1%.

Only in the case of **1**$^-$ is the assignment fully based on experiment, since for this radical anion, which does not contain bridge protons, ring-deuterated derivatives were available.[10] For the remaining radical anions of C_{2v} symmetry, **3**$^-$, **4**$^-$, **5**$^-$, and **7**$^-$, the coupling constants of the ring protons have been assigned by analogy with **1**$^-$. A consistent assignment of the coupling constants to the methine and/or methylene protons in the bridging groups of **3**$^-$, **4**$^-$, **5**$^-$, and **7**$^-$ could be made by comparison of the corresponding values for the four radical anions.

In the case of C_s symmetry, represented by **2**$^-$ and **6**$^-$, the increased number of nonequivalencies leads to some uncertainty in the assignment of the coupling constants. For **2**$^-$, it may be reasonably assumed that the esr data will approximately reflect the relation of this radical anion to **1**$^-$ on one hand, and to **4**$^-$ on the other. This means that the coupling constants should be comparable for similarly located ring and methine protons in the two radical anions. Such an assumption leads to the assignment made in Table I. For **6**$^-$, the replacement of one methine hydrogen by a methyl group gives rise to slightly different coupling constants for the ring protons in positions 2,5 and 9,12 as well as those in 3,4 and 10,11. A precise assignment of these values is, however, of minor importance, since it does not affect the conclusions to be drawn in the present paper.

No assignment has been attempted in the case of **8**$^-$, because the structure of this anti-bridged radical anion precludes a meaningful comparison with its syn counterparts **1**$^-$–**7**$^-$. Nevertheless, symmetry considerations make it probable that all the coupling constants observed for **8**$^-$ should be assigned to five pairs of ring protons (see Discussion).

Coupling constants of ^{13}C nuclei in natural abundance have been measured for three sets of equivalent ring carbon atoms in **1**$^-$ and **4**$^-$. Their assignment is based on the relative intensity of the relevant satellites in the esr spectra and on the results of estimations by current semiempirical formulas.[10,14]

Discussion

Ring Protons. Table II summarizes the coupling constants of the ring protons in the syn-bridged radical anions **1**$^-$–**7**$^-$. In the cases of C_s symmetry, **2**$^-$ and **6**$^-$, the values for the positions 2,5,9,12 and 3,4,10,11 represent the averaged coupling constants for two proton pairs. Table II also lists the analogous values predicted for the ring protons in the radical anion of a planar unbridged [14]annulene. These coupling constants have been obtained from the π-spin populations ρ_μ calculated by means of the McLachlan procedure[15] for the singly occupied perimeter orbital $\psi_S = 0.084\cdot(\phi_1 + \phi_6 + \phi_8 + \phi_{13}) + 0.341(\phi_2 + \phi_5 + \phi_9 + \phi_{12}) - 0.236(\phi_3 + \phi_4 + \phi_{10} + \phi_{11}) - 0.378(\phi_7 + \phi_{14})$ (see also diagrams in Figure 2). The factor $Q_{CH} = -22.5$ G[16] was used in the McConnell[17] relation $a_{H_\mu} = Q_{CH}\cdot\rho_\mu$ to convert the values ρ_μ at the carbon atoms μ into the coupling constants, a_{H_μ}, of the adjacent protons.

Table II. Survey of Ring Proton Coupling Constants (in Gauss) and the Sums of Their Absolute Values for the Radical Anions of Bridged [14]Annulenes **1–8** and of [14]Annulene

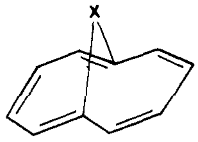
Radical anion of	Coupling constants a_{H_μ} μ = 2,5,9,12	3,4,10,11	7,14	$\sum_\mu \lvert a_{H_\mu}\rvert$
8	*a*	*a*	*a*	11.5[e]
5	(−)2.42	<0.05[b]	(−)2.77	15.2
4	(−)2.78	<0.05[b]	(−)3.44	18.0
3	(−)2.77	<0.05[b]	(−)3.60	18.3
2	(−)2.67[c]	(−)0.36[c]	(−)3.26	18.6
1	(−)2.95	(−)0.37	(−)2.88	19.0
6	(−)3.15[c]	(−)0.50[c]	(−)4.39	23.4
7	(−)3.16	(−)0.81	(−)4.52	24.9
[14]Annulene	−3.42[d]	−0.97[d]	−4.52[d]	26.6

[a] No assignment of coupling constants. [b] Splitting unresolved. [c] Averaged value. [d] Value calculated by the McLachlan procedure. [e] Upper limit, obtained under the assumption that all observed coupling constants can be assigned to ring protons.

McLachlan procedure requires positive signs for the π-spin populations at all carbon atoms μ of [14]annulene which bear ring protons in the bridged derivatives **1**$^-$–**7**$^-$. The pertinent coupling constants a_{H_μ} for the radical anion of [14]annulene should thus be negative, and the same is assumed to be true for the corresponding values listed in Table II.

Two major effects determine the coupling constants a_{H_μ} of the ring protons in **1**$^-$–**7**$^-$: the nonplanarity of the 14-membered perimeter and the electronic substituent effect of the bridging group. Whereas nonplanarity affects the 1s-spin populations at the ring hydrogens without essentially changing the π-spin population ρ_μ at the adjacent carbon atoms μ (see below), the substituent effect gives rise to some redistribution of the π-spin populations themselves. The esr data as presented in Table II are a convenient starting point for the discussion of the two effects.

Nonplanarity. Esr studies[6,7] of the radical anions of bridged [10]annulenes, **10–12**, have shown that deviations of the perimeter from planarity decrease the absolute values of the coupling constants a_{H_μ}.



10 for X = CH_2
11 for X = NH
12 for X = O

The decrease in the values $\lvert a_{H_\mu}\rvert$ has been rationalized as follows.[6,11] In *planar* π radicals the 1s-spin population, which gives rise to a hyperfine splitting by a ring proton, is due to an *indirect* mechanism, the so-called π–σ-spin polarization. This spin population and the ring proton coupling constant a_{H_μ} have, therefore, a sign *opposite* to that of the π-spin population ρ_μ at the adjacent carbon atom μ.[18] On the other hand, in *nonplanar* π radicals, such as the anions of bridged [10]- and [14]annulenes, there is a lack of complete orthogonality between the π system and the C–H σ bonds which permits a *direct* transfer of spin population from the 2pπ orbitals into the 1s orbitals of the ring hy-

---

(13) To save space, the simulated spectra have not been reproduced in the paper.

(14) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961); M. T. Melchior, *ibid.*, **50**, 511 (1969).

(15) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1966); the parameter λ was given its usual value of 1.2.

(16) The value $\lvert Q_{CH}\rvert$ = 22.5 G is equal to the total spectral spread of the benzene radical anion: T. R. Tuttle and S. I. Weissman, *J. Amer. Chem. Soc.*, **80**, 5342 (1958).

(17) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).

(18) H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).

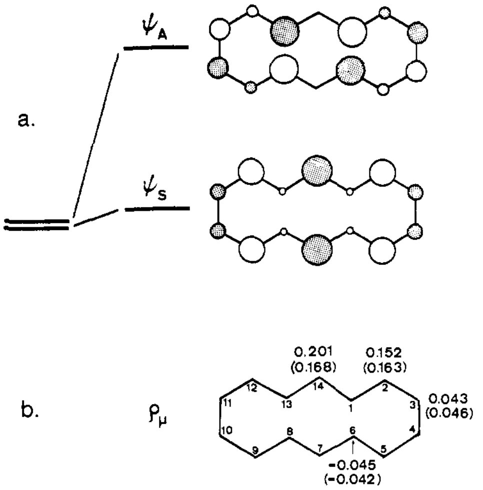


Figure 2. (a) Removal of the degeneracy of the lowest antibonding perimeter orbitals ψ_S and ψ_A[20] by an electron-repelling effect of the bridging groups. In the schematic representation of the two orbitals the areas of the circles are proportional to the squares of the LCAO coefficients; dotted and blank circles symbolize different signs. (b) π-Spin populations ρ_μ calculated by the McLachlan procedure for ψ_S as the singly occupied orbital. Values in parentheses result from adoption of a Coulomb integral $\alpha - 0.5\beta$ for the four bridgehead carbon atoms.

drogens. Since the 1s-spin population brought about by this direct mechanism has the *same* sign as the π-spin population ρ_μ at the carbon atom μ, it will partially cancel the 1s-spin population due to π–σ-spin polarization. As a result, the observed absolute value of the proton coupling constant a_{H_μ} will be reduced.

The general increase in the values $|a_{H_\mu}|$ on going from the top to the bottom of Table II can thus be interpreted by a flattening of the 14-membered perimeter and by the resulting decrease in the *positive* contributions to the *negative* 1s-spin populations at the ring hydrogens. Such an interpretation is supported by the convergence of the coupling constants a_{H_μ} toward the values predicted for the ring protons in the radical anion of planar [14]annulene.

In particular, it is instructive to compare the coupling constants a_{H_μ} for the radical anions **5**$^-$, **4**$^-$, and **6**$^-$ in which the two alkyl bridges are linked by two, one, and no methylene groups, respectively (see also Figure 3). In view of the comparable electronic substituent effect of the alkyl bridges in the three compounds, the regular increase in the values $|a_{H_\mu}|$ on going from **5**$^-$ to **4**$^-$, and to **6**$^-$ can be almost entirely attributed to flattening of the perimeter.

A slightly higher degree of planarity than in **6** should be achieved by the perimeter in the structurally similar compound **7**. The coupling constants of the ring protons in **7**$^-$ are very close to those calculated for the [14]-annulene radical anion.

As a general indicator of the degree of planarity in the whole series **1**–**7** it is convenient to consider the sums $\sum_\mu |a_{H_\mu}|$ listed in the last column of Table II. In this way, slight redistributions of the π-spin populations ρ_μ within a radical anion and the resulting increases in the values $|a_{H_\mu}|$ for some ring protons at the expense of others (see below) can be ignored. Moreover, a consideration of the sums $\sum_\mu |a_{H_\mu}|$, instead of individual coupling constants a_{H_μ}, allows the esr data for the anti-bridged radical anion **8** to be included as well. The deduced sequence of increasing planarity **8** < **5** < **4** ≈ **3** ≈ **2** ≈ **1** < **6** $\gtrless$ **7** (see Table II) compares very well with that suggested by molecular models.

Substituent Effect. Esr spectra of the radical anions **10**$^-$ and **12**$^-$ have indicated that the dominant substituent effect of the alkyl and oxido bridges on the π orbitals of the perimeter in methano- (**10**) and oxido-[10]annulene (**12**) is inductive and electron repelling.[19] The assumption of such an effect for the alkyl and oxido bridges also may be used to interpret the esr data for the radical anions **1**$^-$–**7**$^-$. From a comparison of these data with the diagrams of the degenerate, lowest antibonding perimeter orbitals, ψ_S and ψ_A, depicted in Figure 2a, it is evident that the singly occupied orbital in **1**$^-$–**7**$^-$ strongly resembles ψ_S. The symmetric orbital ψ_S must thus be lower in energy than its antisymmetric counterpart ψ_A.[21] Since ψ_A should be more strongly perturbed by the inductive substituent effect of the bridging groups (*cf.* the squares of the LCAO coefficients at the bridged carbon atoms), the lower energy of ψ_S can be rationalized by the repelling nature of this effect which destabilizes ψ_A to a greater extent than ψ_S (Figure 2a).

The relative strength of the substituent effects of an oxido and an alkyl bridge can be best studied by considering the coupling constants a_{H_μ} for the radical anions **1**$^-$ and **4**$^-$. As established by X-ray analysis of **1**[4] and **4**[5] and as indicated by the sums $\sum_\mu |a_{H_\mu}|$ for **1**$^-$ and **4**$^-$, the perimeter in the two radical anions exhibits a comparable degree of planarity. The differences in the values $|a_{H_\mu}|$ for the corresponding ring protons should thus be interpreted in terms of the different electronic substituent effects of the oxido (**1**) and alkyl bridges (**4**). In a simple inductive HMO model, an electron-repelling effect is simulated by an introduction of a parameter $h < 0$ into the Coulomb integral $\alpha + h\beta$ of the substituted carbon atoms. As shown by the π-spin populations ρ_μ in Figure 2b, such a procedure when applied to the bridged [14]annulenes leads to an increase in the values ρ_μ for μ = 2, 5, 9, 12 and 3, 4, 10, 11 at the expense of ρ_μ for μ = 7, 14. The similar changes observed for the corresponding values $|a_{H_\mu}|$ on passing from **4**$^-$ to **1**$^-$ (see Table II) suggest that an oxido bridge has a stronger repelling effect on the π electrons of the perimeter than an alkyl bridge.[22] An inductive HMO model of **2** based on this suggestion also rationalizes the distribution of π-spin populations ρ_μ in **2**$^-$ and supports the assignment made for the coupling constants of the ring protons in this radical anion.

Replacement of the methylene group linking the two alkyl bridges in **4** by a carbonyl group to yield **3** does

(19) Whereas this evidence for an inductive repelling effect of the alkyl group is in line with generally accepted ideas, the postulation of such an effect for the oxygen atom seems less obvious. It must be assumed that the effect of the oxido bridge in **12** is dominated by the repulsion between the lone pairs of the heteroatom and the π electrons of the perimeter, since the geometry of the bridge impedes the conjugation of the lone pairs with the π system. Such a repulsion (π-inductive effect) can override the attraction of the electronegative heteroatoms which is propagated through the σ bonds (σ-inductive effect).[20]

(20) (a) D. T. Clark, J. N. Murrell, and J. M. Tedder, *J. Chem. Soc.*, 1250 (1963); (b) D. T. Clark, *Chem. Commun.*, 390 (1966); (c) J. H. Hammons, *J. Org. Chem.*, 33, 1123 (1968).

(21) "Symmetric" (S) and "antisymmetric" (A) refer to the mirror plane passing through the carbon atom 7 and 14 and perpendicular to the plane of the perimeter.

(22) D. T. Clark[20b] proposes the parameters h = -0.567 and -0.157 for methoxy and methyl substitution, respectively.

not seem to alter appreciably the substituent effect of the bridges. This conclusion can be drawn from the similar π-spin populations ρ_μ in **4**$^-$ and **3**$^-$, as indicated by the coupling constants a_{H_μ}. Presumably, the influence of the carbonyl group in **3** is sufficiently attenuated by the separating sp^3-hybridized carbon atoms of the alkyl bridges.

Bridge Protons. A further interesting feature of the esr data in Table I is the striking increase in the coupling constants, $a_{\mathrm{H}}^{\mathrm{CH}}$ of the methine protons along the series **5**$^-$, **4**$^-$, and **6**$^-$. The relevant values, 0.47 (**5**$^-$), 0.88 (**4**$^-$), and 2.65 G (**6**$^-$), are in the ratio 1:1.9:5.6. It has already been pointed out that, on going from **5** to **4** and to **6**, the decrease in the number of methylene groups linking the two syn-alkyl bridges leads to a flattening of the 14-membered perimeter. According to molecular models, such a decrease also reduces the dihedral angle θ formed by the 2pπ axis of a bridgehead carbon atom μ and the projection of the C–H methine bond on the plane passing through this axis and perpendicular to C(μ)–C(methine) linkage (Figure 3). From the estimated angles θ = 65 (**5**), 50 (**4**), and 10° (**6**), the respective values $\cos^2\theta$ = 0.18, 0.41, and 0.97 are obtained. Their ratio 1:2.3:5.4 is rather close to that of the coupling constants $a_{\mathrm{H}}^{\mathrm{CH}}$. This correspondence indicates that the coupling constants $a_{\mathrm{H}}^{\mathrm{CH}}$ obey the relation[23] $a_{\mathrm{H}}^{\mathrm{CH}} = B \cdot \rho_\mu \cdot \cos^2\theta$, where the product $|B \cdot \rho_\mu|$ has a similar value for three radical anions. Use of +44.8 G for the parameter B[24] results in the value $|\rho_\mu| \approx 0.06$. It is assumed that in the present case, this value should stand for the sum of the π-spin populations at the two carbon atoms which bear an alkyl bridge in **5**$^-$, **4**$^-$, and **6**$^-$ (μ = 1 and 6, or 8 and 13).[25] The corresponding value $2(-0.045) = -0.09$, calculated by the McLachlan procedure (Figure 2b), is of the same order of magnitude and of negative sign. (Since B is positive, the coupling constants $a_{\mathrm{H}}^{\mathrm{CH}}$ are thus predicted to be negative as well.)

Double Bond Localization. The esr data for the radical anion of *anti*-bismethano[14]annulene **8** require an additional comment. Although no assignment has been made of these data to individual protons, two pieces of information can be obtained from the absolute values of the coupling constants and the number of equivalent protons giving rise to them.

The information deduced from the absolute values has been already considered above. Even under the assumption that all observable values should be assigned to the ten ring protons (*i.e.*, that the splittings due to the four bridge protons are too small to be resolved), the relevant sum $\Sigma_\mu |a_{\mathrm{H}_\mu}|$ would amount to only 11.5 G. This sum is markedly smaller than those found for the radical anions of syn-bridged [14]annulenes, **1**–**7** (see Table II), and complies with the large deviation from planarity expected for the 14-membered perimeter in **8**.

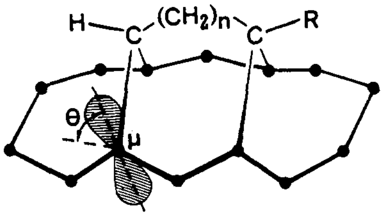
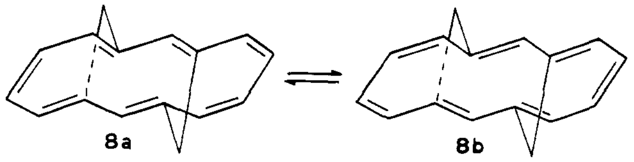


Figure 3. Molecular model showing the dihedral angle θ in the bridged [14]annulenes **5** (n = 2, R = H), **4** (n = 1, R = H), and **6** (n = 0, R = CH$_3$).

The number of equivalent protons yields information about the symmetry of **8**$^-$. The experimental finding that five proton pairs give rise to the observed hyperfine structure rules out C_{2h} symmetry for which at least one of the two sets of four equivalent ring protons (in the positions 2,5,9,12 or 3,4,10,11) should be apparent in the esr data. This finding is not unexpected. Proton resonance spectra of **8** have established that the molecule must be represented by two interconverting structures **8a** and **8b** with localized double bonds.[3]



At −135° the rate of interconversion is sufficiently slow on the nmr time scale for the spectrum to reflect the reduced symmetry (C_s) of a single structure. Evidently, the esr spectrum of the radical anion **8**$^-$ exhibits this behavior even at a higher temperature (−60°), since a smaller decrease in temperature is required on the esr time scale for the observation of the bond localized structure **8a** or **8b**. It would be interesting to study the spectrum of **8**$^-$ at temperatures above −60° as well; unfortunately, the low stability of the radical anions impedes such esr studies.

If a structure **8a** or **8b** of C_s symmetry is adopted for **8**$^-$ at −60°, none of the bridge protons could be pairwise equivalent. It may be therefore argued that (unless the coupling constants of two bridge protons are accidentally equal) none of the observed values should be assigned to these protons. The coupling constants listed for **8**$^-$ in Table I can thus be tentatively assigned to the five pairs of equivalent ring protons.

Acknowledgment. This work was supported by the Schweiz. Nationalfond (Project SR 2.120.69). One of us (K. M.) thanks the Deutsche Forschungsgemeinschaft for a fellowship. We are also obliged to H. Reel for supplying us with samples of **6** and **7** and for some results prior to publication.

---

[23] H. C. Heller and H. M. Connell, *J. Chem. Phys.*, **32**, 1535 (1960); A. Horsfield, J. R. Morton, and D. H. Whiffen, *Mol. Phys.*, **4**, 425 (1961).

[24] A value $\frac{1}{2}|B|$ = 22.4 G has been found in the esr study of the radical anions of disubstituted dimethylnaphthalenes: F. Gerson, E. Heilbronner, and B. Weidmann, *Helv. Chim. Acta*, **47**, 1951 (1964); see also F. Gerson, ref 9, p 107.

[25] See, however, D. H. Whiffen, *Mol. Phys.*, **6**, 223 (1963).