43. The Radical Anions of *syn*-1,6:8,13-Bridged [14]Annulenes. A Compilation of Hyperfine Data

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Hyperfine coupling constants and g-factors determined by ESR and ENDOR spectroscopy are given for the radical anions of 21 *syn*-1,6:8,13-bridged [14]annulenes. The great majority of these values is reported for the first time. The hyperfine data are consistent with the single occupancy of an orbital which resembles a π-perimeter-LUMO of the same nodal properties. The sum of the coupling constants of the protons attached to the π-perimeter can be used as a planarity criterion for this perimeter.

Introduction. – Some years ago, we described the ESR spectra of the radical anions of 7 *syn*-1,6:8,13-bridged [14]annulenes, **3**, **5**, **8**, **10**, **11**, **20**, and **21** [1]. Since then, many further representatives of this class of compounds have been synthesized [2] [3]. We now report the ESR-spectroscopic data for the radical anions of additional 14 *syn*-1,6:8,13-bridged [14]annulenes, **1**, **2**, **4**, **6**, **7**, **9**, and **12**–**19**. Also with one exception[2]), the formerly studied ESR spectra [1] have been reexamined at an improved resolution and with the aid of the ENDOR technique. The higher precision thus achieved has led to slight modifications of the previously reported coupling constants. Some reassignments of these values have been indicated by the comparison with the hyperfine data now available for the whole series. g-Factors, which were not determined in [1], are now reported for all but one[2]) radical anions.

In addition to their use as reference data, the vast number of ring-proton coupling constants presented here provides an enlarged testing ground for the proposed role of these values as a planarity criterion [1].

Results and Discussion. – The experimental data for the radical anions $\mathbf{1}^{\overline{\cdot}}$–$\mathbf{21}^{\overline{\cdot}}$ are listed in the *Table*. Again, with the exception of $\mathbf{11}^{\overline{\cdot}}$ which was previously generated by electrolytic reduction [1][2]), all values refer to radical anions prepared by reaction of the corresponding neutral compounds with K metal in 1,2-dimethoxyethane (DME). The data were determined from ESR and proton ENDOR spectra taken in the range of 183–203 K[3]). An illustrative example is provided in *Fig. 1* by the spectra of $\mathbf{12}^{\overline{\cdot}}$ which is the radical anion with the largest number of different sets of magnetic nuclei (5 pairs of equivalent protons, 3 single protons and one ^{14}N-nucleus). For the paramagnetic species

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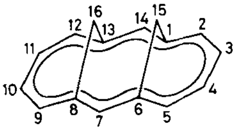
[1]) Present address: *Ilford AG*, CH–1701 Fribourg.

[2]) The radical anion $\mathbf{11}^{\overline{\cdot}}$ has not been reinvestigated for want of the starting material **11**.

[3]) A *Varian-E9* ESR spectrometer coupled to a *Varian-ENDOR-1700* System was used.



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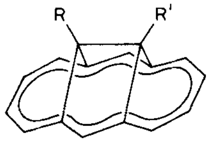

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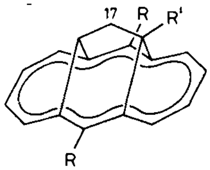
3 R = H, R' = Me
4 R = R' = Me



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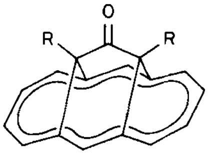
6 R = Me, R' = H
7 R = H, R' = Me



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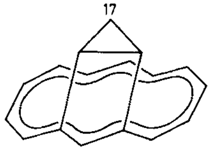
9 R = Me



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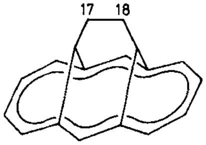

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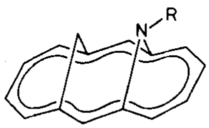

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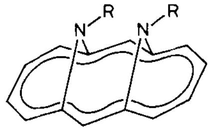
12-D R = D



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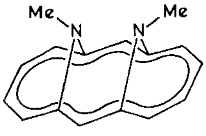
13-D_2 R = D



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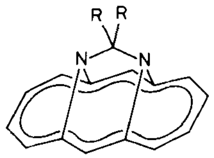
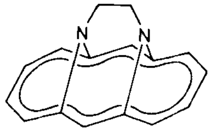


15 R = H
15-D_2 R = D
16 R = Me



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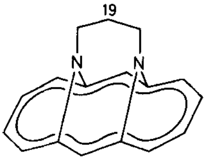

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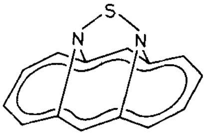

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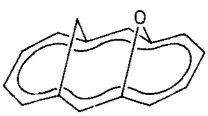

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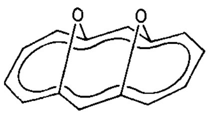

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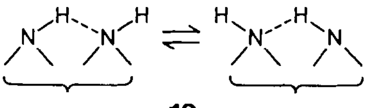
obtained upon reduction of **13**, the notation $\mathbf{13}^{\cdot-}$ has been used throughout the paper, although this species may, in fact, be the radical dianion $\mathbf{13}^{\cdot=}$. Loss of one H-atom at the imino-bridging groups and the formation of $\mathbf{13}^{\cdot=}$ are indicated by the observation of a hyperfine splitting from only *one* NH-proton. The effective symmetry D_{2h} can be accounted for by a rapid oscillation of this proton between two equivalent sites at the

Table. *^{1}H- and ^{14}N-Coupling Constants* (in mT[a]), *and g-Factors*[b]) *for the Radical Anions of the 1,6:8,13-Bridged [14]Annulenes,* **1**–**21**

μ[c]	2,5,9,12	3,4,10,11	7,14	15,16	17,18	S[d]	g
1$^{\cdot-}$	0.239 (4H)	0.026 (4H)	0.281 (2H)	0.102 (2H)[e] 0.048 (2H)[f]	–	1.62	2.0030
2$^{\cdot-}$	0.323 (4H)	0.040 (4H)	0.446 (2H)	0.265 (2H)	–	2.34	2.0028
3$^{\cdot-}$	0.323 (2H)[g] 0.312 (2H)[i]	0.054 (2H)[h] 0.041 (2H)[j]	0.443 (2H)	0.267 (1H) < 0.008 (3H)[k]	–	2.35	2.0028
4$^{\cdot-}$	0.305 (4H)	0.053 (4H)	0.420 (2H)	< 0.008 (6H)[k]	–	2.27	2.0028
5$^{\cdot-}$	0.280 (4H)	0.010 (4H)	0.341 (2H)	0.088 (2H)	< 0.008 (2H)	1.84	2.0028
6$^{\cdot-}$	0.322 (4H)	0.010 (4H)	0.310 (6H)[k]	0.099 (2H)	< 0.008 (2H)	–	2.0028
7$^{\cdot-}$	0.288 (2H)[g] 0.221 (2H)[i]	0.037 (2H)[h] < 0.008 (2H)[j]	0.298 (2H)	0.115 (1H) 0.014 (3H)[k]	< 0.008 (2H)	1.69	2.0029
8$^{\cdot-}$	0.279 (4H)	< 0.008 (4H)	0.355 (2H)	0.095 (2H)	–	1.83	2.0028
9$^{\cdot-}$	0.197 (4H)	0.059 (4H)	0.252 (2H)	0.009 (6H)[k]	–	1.53	2.0030
10$^{\cdot-}$	0.321 (4H)	0.078 (4H)	0.461 (2H)	–	0.028 (2H)	2.52	2.0027
11$^{\cdot-}$	0.242 (4H)	< 0.008 (4H)	0.277 (2H)	0.047 (2H)	0.018 (4H)	1.52	[l]
12$^{\cdot-}$	0.285 (2H)[i] 0.238 (2H)[g]	0.027 (2H)[j] 0.023 (2H)[h]	0.337 (2H)	0.102 (1H)[e] 0.043 (1H)[f] 0.059 (1H)[m] 0.057 (1N)	–	1.82	2.0029
13$^{\cdot-}$[n]	0.293 (4H)	0.022 (4H)	0.265 (2H)	0.030 (2N) 0.057 (1H)[m]	–	1.79	2.0028
14$^{\cdot-}$	0.244 (4H)	0.063 (4H)	0.204 (2H)	0.040 (2N) 0.021 (6H)[k]	–	1.64	2.0029
15$^{\cdot-}$	0.279 (4H)	< 0.008 (4H)	0.318 (2H)	0.017 (2N)	0.017 (2H)[m]	1.75	2.0026
16$^{\cdot-}$	0.271 (4H)	< 0.008 (4H)	0.321 (2H)	0.046 (2N)	< 0.008 (6H)[k]	1.73	2.0027
17$^{\cdot-}$	0.237 (4H)	< 0.008 (4H)	0.312 (2H)	0.017 (2N)	0.014 (4H)	1.57	2.0029
18$^{\cdot-}$	0.252 (4H)	< 0.008 (4H)	0.303 (2H)	0.022 (2N)	0.032 (4H)[o]	1.61	2.0028
19$^{\cdot-}$	0.252 (4H)	< 0.008 (4H)	0.313 (2H)	0.019 (2N)	–	1.63	2.0029
20$^{\cdot-}$	0.296 (2H)[i] 0.228 (2H)[g]	0.045 (2H)[h] 0.026 (2H)[j]	0.334 (2H)	0.094 (1H)[e] 0.045 (1H)[f]	–	1.86	2.0027
21$^{\cdot-}$	0.297 (4H)	0.036 (4H)	0.289 (2H)	–	–	1.91	2.0026

[a] Exper. error: ± 1%. [b] Exper. error: ± 0.0001. [c] Position. [d] *Cf. Text* for definition of S. [e] *exo*-Protons of the CH_2-groups. [f] *endo*-Protons of the CH_2-groups. [g] μ = 9,12. [h] μ = 3,4. [i] μ = 2,5. [j] μ = 10,11. [k] Protons of the CH_3 substituents. [l] Not determined; *cf. Footnote 2.* [m] Protons of the NH groups; assignments confirmed by deuteriation. [n] Presumably radical dianion, **13**$^{\cdot=}$; *cf. Text.* [o] The hyperfine splittings from two further protons in the position 19 of **18**$^{\cdot-}$ are unresolved (< 0.008 mT).



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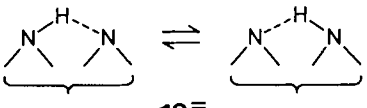

13$^{\cdot=}$

N-atoms in a way analogous to the wind-shield wiper flip found for two NH-proton in the neutral compound **13** [3].

Assignments of the coupling constants to sets of equivalent protons in **1**$^{\cdot-}$–**21**$^{\cdot-}$ are based on a combination of experimental evidence (multiplicities, specific deuteriation or methylation), MO-theoretical arguments and internal consistency of the data. The underlying MO model has recently been discussed in full length [4]. It implies that the frontier orbitals of the 1,6:8,13-bridged [14]annulenes can be correlated with the MO's of the 14-membered π-perimeter. *Fig. 2* depicts the degenerate lowest antibonding perimeter-

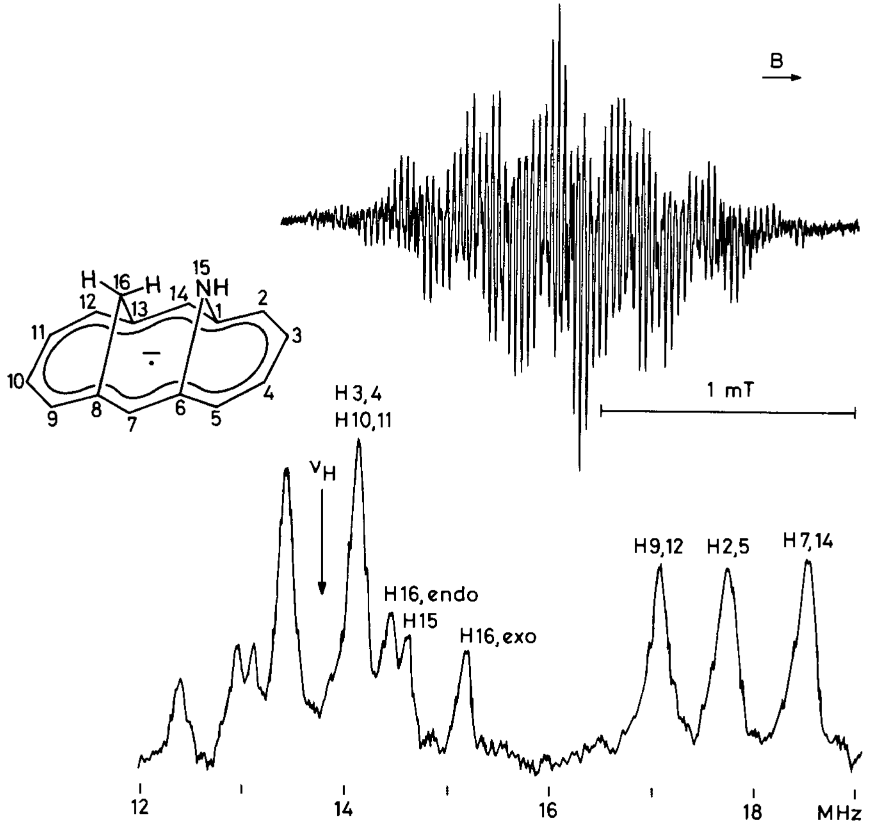

Fig. 1. *ESR and proton ENDOR spectra of the radical anion of 1,6-imino-8,13-methano[14]annulene* (**12**). Solvent: DME; counterion: K^+; temp. 193 K. ν_H = frequency of the free proton.

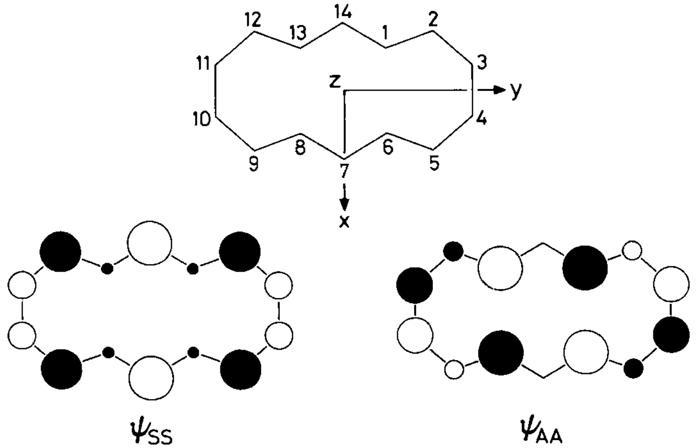

Fig. 2. *The degenerate lowest unoccupied MO's (LUMO's) of the 14-membered π-perimeter.* The areas of the circles are proportional to the squares of the LCAO coefficients. Filled and blank circles symbolize opposite signs of these coefficients. The shape of the perimeter and the numbering of the π-centres are adapted to the 1,6:8,13-bridged [14]annulenes **1**–**21**.

MO's, ψ_{SS} and ψ_{AA}, which are relevant to the discussion of the π-spin distribution in the radical anions. (ψ_{SS} is symmetric and ψ_{AA} is antisymmetric with respect to the mirror planes xz and yz.) The hyperfine data for all radical anions, $\mathbf{1}^{\cdot-}$–$\mathbf{21}^{\cdot-}$, are consistent with the single occupancy of a ψ_{SS}-like orbital which must, therefore, lie below a ψ_{AA}-like one. This energy sequence is readily rationalized in terms of inductive perturbations by the bridging groups and homoconjugative interactions between the formally non-bonded but spatially proximate bridged centres [4]. Both effects should strongly destabilize ψ_{AA}, whereas ψ_{SS} is expected to be only marginally affected.

Although the singly occupied orbital of $\mathbf{1}^{\cdot-}$–$\mathbf{21}^{\cdot-}$ correlates with the perimeter-LUMO (ψ_{SS}) of the same nodal properties, the coupling constants, a_{H_μ}, of the protons attached to the π-centres μ vary markedly along the series. It has been convincingly demonstrated [1] that these values are very sensitive to the deviations of the perimeter from planarity. Such deviations permit a direct spin transfer onto the H-atoms and, since the 1s-spin population brought about by this mechanism has a sign opposite to that arising from π–σ spin polarization [5], the absolute values $|a_{H_\mu}|$ are reduced. The sum $S = \sum_\mu |a_{H_\mu}|$ over all proton-bearing centres μ of the perimeter has therefore been proposed as a planarity criterion [1]; the larger S, the more flattened is the 14-membered π-perimeter. By inspecting the S-values *(Table)* conclusions can thus be drawn with respect to the relative distortions of the perimeter in $\mathbf{1}^{\cdot-}$–$\mathbf{21}^{\cdot-}$. Such conclusions are in general agreement with the geometry of **1**–**21**, as deduced from molecular models and as confirmed in numerous cases by an X-ray analysis [6] [7]. Several comments on the S-values in the light of their role as a planarity criterion are presented below.

i) The rather low S-value of $\mathbf{1}^{\cdot-}$ (1.62 mT) points to a substantial bending of the perimeter, the distortion being clearly the consequence of a severe steric interference by the *endo*-H-atoms of the bridging methano groups.

ii) The most effective way to flatten the perimeter is to eliminate the *endo*-H-atoms by a C(15)–C(16) bond, as shown by the high S-values of $\mathbf{2}^{\cdot-}$ (2.34 mT), $\mathbf{3}^{\cdot-}$ (2.35 mT), $\mathbf{4}^{\cdot-}$ (2.27 mT), and, in particular, of $\mathbf{10}^{\cdot-}$ (2.52 mT).

iii) Less effective in this respect is the substitution of one or both methano by imino or oxido groups, which is realized in $\mathbf{12}^{\cdot-}$ (1.82 mT), $\mathbf{13}^{\cdot-}$ (1.79 mT), $\mathbf{20}^{\cdot-}$ (1.86 mT) and $\mathbf{21}^{\cdot-}$ (1.91 mT). Evidently the steric interference by the *endo*-H-atoms is alleviated but not removed on replacing them by the lone pairs associated with the N- or O-atoms.

iv) As indicated by the lower S-values of $\mathbf{11}^{\cdot-}$ (1.52 mT) and $\mathbf{17}^{\cdot-}$ (1.57 mT) relative to those of $\mathbf{5}^{\cdot-}$ (1.84 mT) and $\mathbf{15}^{\cdot-}$ (1.75 mT), respectively, the perimeter becomes increasingly distorted when the C(15)- and C(16)- or N(15)- and N(16)-atoms of the bridging groups are joined by *two* instead of *one* methylene links.

v) Further reduction in the S-value is, however, not observed on going from $\mathbf{17}^{\cdot-}$ (1.57 mT) to $\mathbf{18}^{\cdot-}$ (1.61 mT), *i.e.*, on replacing the *di*- by a *tri*methylene chain. As confirmed by an X-ray analysis of **18** [7], an excessive bending of the perimeter is avoided due to a substantial flattening at the N(15)- and N(16)-atoms and a marked enlargement of the C(1)–N(15)–C(6) and C(8)–N(16)–C(13) angles.

vi) Whereas the replacement of the CH_2 link in $\mathbf{5}^{\cdot-}$ (1.84 mT) by a CO group, to yield $\mathbf{8}^{\cdot-}$ (1.85 mT), has no effect on the S-value, dimethyl substitution of the C(15)- and C(16)-atoms in $\mathbf{8}^{\cdot-}$, leading to $\mathbf{9}^{\cdot-}$ (1.53 mT), strongly reduces this value. The markedly increased deviations of the perimeter from planarity, predicted therewith for $\mathbf{9}^{\cdot-}$, awaits a verification by an X-ray analysis of **9**.

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REFERENCES

[1] F. Gerson, K. Müllen, E. Vogel, *J. Am. Chem. Soc.* **1972,** *94,* 2924.

[2] For a review see: E. Vogel, *Pure Appl. Chem.* **1982,** *54,* 1015.

[3] For most recent work see: E. Vogel, F. Kuebart, J. A. Marco, R. Andree, H. Günther, R. Aydin, *J. Am. Chem. Soc.* **1983,** *105,* 6982; R. Andree, Diplomarbeit, Universität Köln, 1982.

[4] F. Gerson, W. Huber, J. Lopez, *J. Am. Chem. Soc.* **1984,** *106,* 5808.

[5] See, *e.g.*, F. Gerson, 'High Resolution ESR Sepctroscopy', Verlag Chemie, Weinheim, and J. Wiley, New York, 1970.

[6] For a review see: M. Simonetta, *Pure Appl. Chem.* **1980,** *52,* 1597.

[7] R. Destro, T. Pilati, M. Simonetta, E. Vogel, *J. Am. Chem. Soc.*, submitted for publication.