Acknowledgment. We are grateful to Professor Andrew Streitweiser for helping us generate our bending vibration explanation of hyperconjugative isotope effects, and we also thank the Natural Sciences and Engineering Research Council of Canada and donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

Registry No. $(CH_3)_2COH^+$, 43022-03-3; 2,4,6-$(CH_3)_3C_6H_2COCH_3$, 1667-01-2; $(CH_3)_2CO$, 67-64-1; $(CH_3)_3CCOCH_3$, 75-97-8; CH_3CHO, 75-07-0; C_6H_5-$COCH_3$, 98-86-2; $CH_3CO_2H_2^+$, 18639-92-4; CH_3CO_2H, 64-19-7; $CH_3COOC_6H_5$, 122-79-2; CH_3COCl, 75-36-5; 2,4-$(NO_2)_2C_6H_3NHN{=}C(CH_3)_2$, 1567-89-1; $(CH_3)_2C{=}CHCH_3$, 513-35-9; $CH_3CH{=}CHC_6H_5$, 637-50-3; $(CH_3)_2C{=}C(CH_3)_2$, 563-79-1; 2,4-$(NO_2)_2C_6H_3NHN{=}C(CD_3)_2$, 92350-12-4; $(CD_3)_2C{=}CHCH_3$, 1787-45-7; $(CD_3)_2C{=}C(CH_3)_2$, 38132-23-9; $(CD_3)_2C(OH)CH_2CH_3$, 75295-95-3; $(CD_3)_2C(OH)CH(CH_3)_2$, 104977-32-4; $C_6H_5COCD_3$, 17537-31-4; C_6H_5OH, 108-95-2; $(C_2H_5O)_2CHCD_3$, 92144-49-5; CD_3CHO, 19901-15-6; $C_6H_5COCD_3$, 17537-31-4; 2,4,6-$(CH_3)_3C_6H_2COCl_3$, 59660-67-2; (*E*)-$C_6H_5CH{=}CHCD_3$, 104977-33-5; $C_6H_5C{\equiv}CCD_3$, 71257-77-7; CD_3COOD, 1186-52-3; CD_3CO_2H, 1112-02-3; CD_3COCl, 19259-90-6; D_2, 7782-39-0; acetone-d_6, 666-52-4; methyl-d_3 iodide, 865-50-9; triethyl orthoformate, 122-51-0; phenylacetylene, 536-74-3.

Supplementary Material Available: Table of NMR data (1 page). Ordering information is given on any current masthead page.

The Radical Anion of Homoazulene and Its Rearrangement Products. An ESR and ENDOR Study

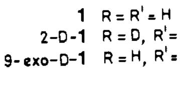
Fabian Gerson,*[1a] Jürgen Knöbel,[1a,c] André Metzger,[1a,d] Lawrence T. Scott,[1b] Mark A. Kirms,[1b] Mitsunori Oda,[1b] and Chris A. Sumpter[1b]

Contribution from the Institut für Physikalische Chemie der Universität Basel, CH-4056 Basel, Switzerland, and Department of Chemistry, University of Nevada, Reno, Nevada 89557.

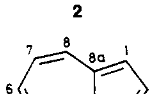
Received May 14, 1986

Abstract: The radical anions of homoazulene (1,5-methano[10]annulene, **1**) and two of its deuterio derivatives have been studied by ESR and, in part, by ENDOR spectroscopy. The compound **1** is reduced to the radical anion at less negative potential ($E_{1/2} = -1.94$ V) than the isomeric 1,6-methano[10]annulene (**2**) (−2.21 V), but $\mathbf{1}^{\bullet-}$ is markedly less persistent than $\mathbf{2}^{\bullet-}$. The most prominent hyperfine feature of $\mathbf{1}^{\bullet-}$ is the very large splitting (1.342 mT) from the exo proton in the methano bridging group. The next largest coupling constants (0.685 and 0.432 mT) are due to the protons at the π-centers situated in the mirror plane (m) of **1**. Both the $E_{1/2}$ value of **1** and the hyperfine data for $\mathbf{1}^{\bullet-}$ indicate that the SOMO in $\mathbf{1}^{\bullet-}$ correlates with one of the lowest antibonding perimeter MO's (ψ_S) which is symmetric with respect to the plane m. The decrease in energy of ψ_S relative to its antisymmetric counterpart (ψ_A) is attributed to homoconjugation which should be particularly favored in **1** by deviations of the perimeter from planarity. The dominant role of homoconjugation in removing the degeneracies of the perimeter MO's accounts for the similarities in the coupling constants of the protons which are attached to the corresponding π-centers in $\mathbf{1}^{\bullet-}$ and in the radical anion of azulene (**3**). Nonplanarity of the π-system seems to have a less profound effect on the coupling constants of these protons in $\mathbf{1}^{\bullet-}$ than it has on the analogous values for the isomeric $\mathbf{2}^{\bullet-}$. The different nodal properties of the SOMO's, a ψ_S-like MO in $\mathbf{1}^{\bullet-}$ and a ψ_A-like one in $\mathbf{2}^{\bullet-}$, are invoked to provide a rationalization of this finding. The primary radical anion $\mathbf{1}^{\bullet-}$ readily rearranges into secondary reduction products having the carbon frameworks of bicyclo[5.4.0]undeca-1,3,5,7,9-pentaenyl (benzotropyl, **4**) or bicyclo[6.3.0]undeca-1,3,5,7,9-pentaenyl (**5**), so that the corresponding radical dianions, $\mathbf{4}^{\bullet 2-}$ or $\mathbf{5}^{\bullet 2-}$, are obtained as the final paramagnetic species. Whereas $\mathbf{4}^{\bullet 2-}$ has been known from previous studies, characterization of $\mathbf{5}^{\bullet 2-}$ by ESR and ENDOR spectroscopy is reported only in the present work. A reaction mechanism is suggested for the conversion of $\mathbf{1}^{\bullet-}$ into each of the two radical dianions.

Homoazulene (1,5-methano[10]annulene or bicyclo[5.3.1]-undeca-1,3,5,7,9-pentaene, **1**) was synthesized a few years ago by two research groups.[2] It is an isomer of 1,6-methano[10]-annulene (bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene, **2**) which has been known since 1964.[3] Although **1**, like its isomer **2**, exhibits properties attributable to cyclic conjugation, such as an induced diamagnetic ring current,[4] it strongly differs from **2** in its physical and chemical properties. Deviations of the ten-membered π-perimeter from planarity should be much more pronounced in **1** than in **2**. Particularly, the largest dihedral angle between the 2p axes at the consecutive carbon π-centers in **1** is predicted to be 54° by molecular mechanics,[5] whereas the analogous angle in a derivative of **2** is 34°, as determined by an X-ray crystallographic structure analysis.[6] The substantially lower resonance energy of **1** relative to **2** (27 vs. 72 kJ/mol)[7] is reflected by a higher



1 R = R' = H
2-D-**1** R = D, R' = H
9-*exo*-D-**1** R = H, R' = D



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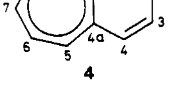

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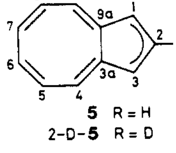

5 R = H
2-D-**5** R = D

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[1] (a) Universität Basel. (b) University of Nevada. (c) Present address: F. Hoffmann-La Roche & Cie SA, CH-4002 Basel. (d) Present address: Ciba-Geigy, CH-4133 Schweizerhalle.

[2] (a) Masamune, S.; Brooks, D. W. *Tetrahedron Lett.* **1977**, 3239. (b) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *Angew. Chem.* **1981**, *93*, 282; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 274.

[3] Vogel, E.; Roth, H. D. *Angew. Chem.* **1964**, *76*, 145; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 228. Vogel, E. *Chem. Soc. Spec. Publ.* **1967**, *21*, 113.

[4] Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* **1981**, *103*, 5216.

[5] Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893.

[6] Dobler, M.; Dunitz, J. D. *Helv. Chim. Acta* **1965**, *48*, 1429.

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reactivity and a lesser propensity to electrophilic substitution.

Another consequence of the stronger bending of the ten-membered π-perimeter in **1** is a larger overlap of the 2p AO's at the formally nonbonded but spatially proximate bridged carbon atoms. Homoconjugation should thus be more important for **1** than for **2**. In fact, **1** mimics azulene (**3**) in some of its properties; for instance, the positions of the long-wave band in the electronic spectra of **1**[8] and its derivatives follow Plattner's rules[9] for substituted azulenes.

While the radical anion **2**$^{\bullet-}$ has been dealt with in a number of publications[10-12] during the last two decades, studies of **1**$^{\bullet-}$ have not yet been reported. An investigation of **1**$^{\bullet-}$ by ESR spectroscopy is of interest for several reasons.

(i) The singly occupied molecular orbital (SOMO) in **1**$^{\bullet-}$ should resemble that one of the two degenerate lowest antibonding MO's of the 10-membered π-perimeter which is more stabilized or less destabilized than its counterpart by the introduction of the methano bridging group. The nodal properties of the SOMO can thus provide information about the perturbations exerted on these MO's by the bridging group.[10a,12,13]

(ii) If homoconjugation is the dominant perturbation removing the degeneracy of the lowest antibonding perimeter MO's, the SOMO in **1**$^{\bullet-}$ should correlate with the corresponding MO in **3**$^{\bullet-}$, i.e., the spin distributions over the 10 π-centers should follow the same pattern in **1**$^{\bullet-}$ and **3**$^{\bullet-}$.

(iii) Since deviations of the π-perimeter from planarity in bridged annulenes lead to a breakdown of the π–σ separation, the coupling constants of the protons at the π-centers in **1**$^{\bullet-}$ may markedly differ from the values expected for a planar π-radical anion.[10,14]

(iv) The primary radical anion **1**$^{\bullet-}$ should be prone to rearrangements yielding secondary products, as previously found for **2**$^{\bullet-}$ and structurally related species.[11,15]

The present work explores these points of interest by applying ESR and, in part, ENDOR spectroscopy, to the radical anions of **1** and its deuterio derivatives, 2-D-**1** and 9-exo-D-**1**. Also investigated are the secondary reduction products, in which the carbon framework of **1** rearranges into those of bicyclo[5.4.0]-undeca-1,3,5,7,9-pentaenyl (benzotropyl, **4**) or bicyclo[6.3.0]-undeca-1,3,5,7,9-pentaenyl (**5**). These products have been identified by ESR and ENDOR spectroscopy in form of the corresponding radical dianions, **4**$^{\bullet 2-}$ or **5**$^{\bullet 2-}$.

Results

The Radical Anion of Homoazulene (1). In contrast to the isomeric compound **2**, which is reversibly reduced at a half-wave potential $E_{1/2} = -2.21$ V (vs. SCE),[16] the cyclic voltammogram of **1** displays an irreversible reduction wave at −1.97 V.[17] The electrochemical behavior thus indicates a greater ease of formation and a considerably lower kinetic stability (persistence) of **1**$^{\bullet-}$ relative to **2**$^{\bullet-}$. In fact, because of the short lifetime of **1**$^{\bullet-}$, its ESR spectrum could hardly be observed when this radical anion was prepared by the same procedure as **2**$^{\bullet-}$, i.e., by reaction of the neutral compound with potassium in an ethereal solvent, such as 1,2-dimethoxyethane (DME) or 2-methyltetrahydrofuran (MTHF). However, addition of hexamethylphosphoric acid triamide (HMPT) to DME or MTHF greatly enhanced the persistence of **1**$^{\bullet-}$, so that fairly intense and well-resolved ESR spectra were obtained with these solvent mixtures at low temperatures. Figure 1 shows such a spectrum taken in MTHF/HMPT (5:1 by volume) at 163 K ($g = 2.0031 \pm 0.0001$). The simulated derivative curve, also reproduced in Figure 1, was computed by the use of the following coupling constants: 1.342 ± 0.008, 0.685 ± 0.005, 0.432 ± 0.003, and 0.045 ± 0.001 mT, each from a single proton, in addition to 0.367 ± 0.003, 0.328 ± 0.003, and 0.091 ± 0.001 mT, each from a pair of equivalent protons. Except for 0.432 mT which had to be replaced by a deuteron coupling constant of 0.067 ± 0.001 mT, these values are likewise appropriate for 2-D-**1**$^{\bullet-}$. Figure 2 presents the observed and simulated ESR spectra of 2-D-**1**$^{\bullet-}$, along with the corresponding proton ENDOR signals. Being associated with five out of seven coupling constants found for the parent radical anion **1**$^{\bullet-}$, these signals provide an additional check for the analysis of the hyperfine patterns in the ESR spectra of both **1**$^{\bullet-}$ and 2-D-**1**$^{\bullet-}$. (The ENDOR signals are missing for the coupling constants of 0.432 and 1.342 mT; the former value belongs to the proton in the deuterated 2-position, while the latter is too large to be determined in the frequency range accessible to the ENDOR system used in this study.)

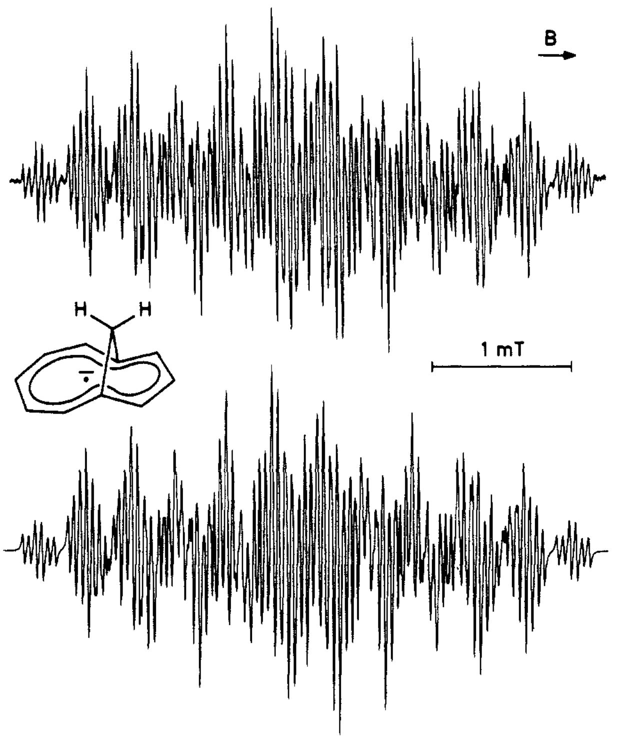

Figure 1. Top: ESR spectrum of **1**$^{\bullet-}$. Solvent, MTHF/HMPT (5:1); counterion, K$^+$; temperature, 163 K. Bottom: computer simulation. Coupling constants, see text; line shape, Lorentzian; line width, 0.025 mT.

The successful application of the ENDOR technique to 2-D-**1**$^{\bullet-}$, as contrasted with its failure for **1**$^{\bullet-}$, is presumably due to the different degrees of purity of the starting material which was available as dilute solutions of the respective neutral compounds in pentane (see Experimental Section). In this regard, the solutions of 2-D-**1** were superior to those of **1**. As for the second deuterated derivative, 9-exo-D-**1**, its solutions in pentane contained a considerable amount of hardly removable impurities which impaired the achievement of high resolution in the ESR spectrum of the radical anion. Despite this handicap, the observed spectrum of 9-exo-D-**1**$^{\bullet-}$ could be satisfactorily fitted by a computer simulation when use was made of the hyperfine data for **1**$^{\bullet-}$ with the largest coupling constant of 1.342 mT being replaced by a splitting of 0.205 ± 0.010 mT from one deuteron.

Assignments of the coupling constants (in mT) to protons in the individual positions of **1**$^{\bullet-}$ are indicated in the diagram below.

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(7) Roth, W. R.; Böhn, M.; Lennartz, H.-W.; Vogel, E. *Angew. Chem.* **1983**, *95*, 1011; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1007.

(8) Scott, L. T.; Oda, M.; Erden, I. *J. Am. Chem. Soc.* **1985**, *107*, 7213.

(9) See, e.g., Heilbronner, E. In *Nonbenzenoid Aromatic Hydrocarbons*; Ginsburg, D., Ed.; Interscience: New York, 1959; Chapter 5.

(10) (a) Gerson, F.; Heilbronner, E.; Böll, W. A.; Vogel, E. *Helv. Chim. Acta* **1965**, *48*, 1494. (b) Gerson, F.; Müllen, K.; Vogel, E. *Ibid.* **1971**, *54*, 2731. (c) Gerson, F.; Müllen, K.; Wydler, Ch. *Ibid.* **1976**, *59*, 1371.

(11) Gerson, F.; Huber, W.; Müllen, K. *Helv. Chim. Acta* **1979**, *62*, 2109.

(12) See, also: Gerson, F.; Hammons, J. H. In *Nonbenzenoid Aromatics*; Snyder J. P., Ed.; Academic Press: New York, 1971; Vol. II, Chapter 2.

(13) Gerson, F.; Huber, W.; Lopez, J. *J. Am. Chem. Soc.* **1984**, *106*, 5808.

(14) Gerson, F.; Müllen, K.; Vogel, E. *J. Am. Chem. Soc.* **1972**, *94*, 2924. Gerson, F.; Knöbel, J.; Lopez, J.; Vogel, E. *Helv. Chim. Acta* **1985**, *68*, 371.

(15) Gerson, F.; Huber, W.; Müllen, K. *Angew. Chem.* **1978**, *90*, 216; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 208.

(16) Huber, W., unpublished results.

(17) Solvent, *N,N*-dimethylformamide; supporting salt, 0.1 M Et_4NBF_4; working electrode, hanging mercury drop electrode; auxiliary electrode, platinum wire; temperature, 298 K; scan 1 V/s.

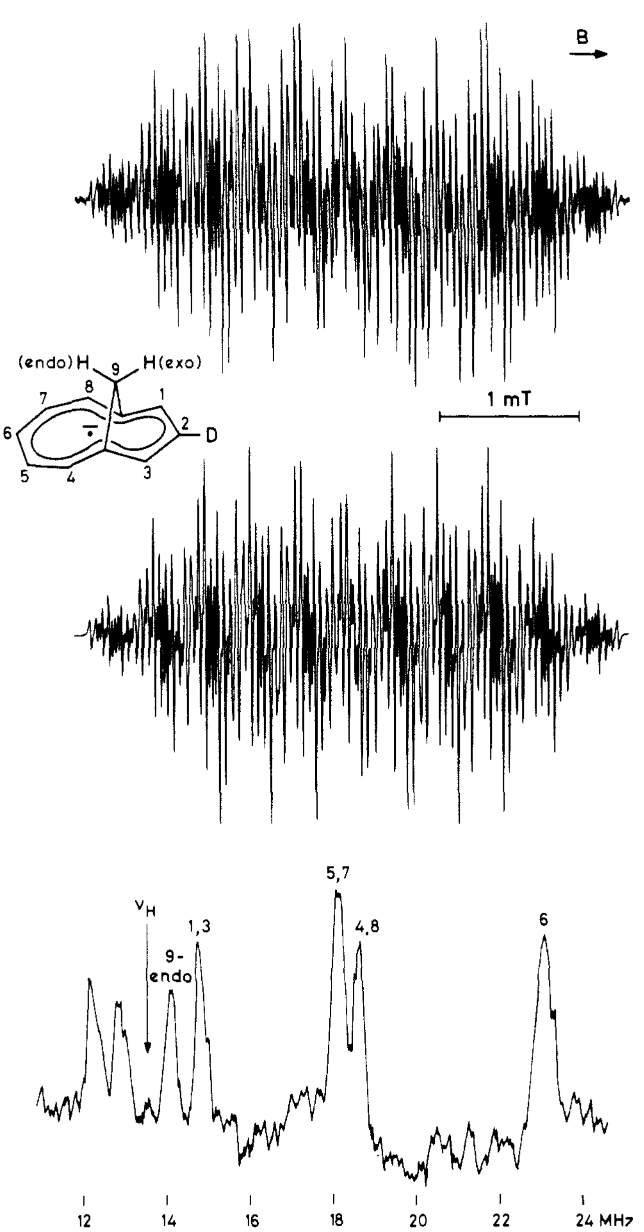
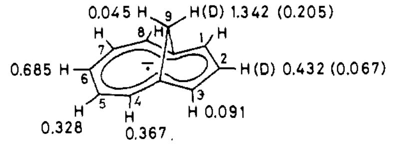


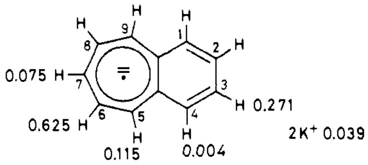
Figure 2. Top: ESR spectrum of 2-D-$1^{\bullet-}$. Solvent, MTHF/HMPT (5:1), counterion, K^+; temperature, 183 K. Middle: computer-simulation. Coupling constants, see text; line shape, Lorentzian; line width, 0.020 mT. Bottom: proton ENDOR spectrum of 2-D-$1^{\bullet-}$. Experimental conditions as for the ESR spectrum. ν_H = frequency of the free proton. The numbers above the ENDOR signals denote the positions of the protons assigned to these signals.

Wherever such assignments do not follow from experiment, they are based on arguments presented in the Discussion.



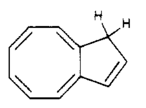
Secondary Reduction Products of 1. The radical anion $1^{\bullet-}$, which is the primary product of the reaction of 1 with potassium metal, easily converts into molecular species having a rearranged carbon framework. Two such species were identified by virtue of their paramagnetism: the isomeric radical dianions, $4^{\bullet 2-}$ and $5^{\bullet 2-}$, of bicyclo[5.4.0]undeca-1,3,5,7,9-pentaenyl (benzotropyl, **4**) and bicyclo[6.3.0]undeca-1,3,5,7,9-pentaenyl (**5**), respectively.

As stated in the preceding section, $1^{\bullet-}$ had rather a short lifetime when prepared in neat DME or MTHF, i.e., in the absence of HMPT. Exhaustive reduction of 1 with potassium metal in these solvents at 193 K yielded a persistent paramagnetic species (g = 2.0027 ± 0.0001) of which the ESR and ENDOR spectra were readily recognized as those of $4^{\bullet 2-}$. Although this radical dianion had been known since 1967,[18] it was correctly and completely characterized only several years ago.[11,19] The pertinent coupling constants (in mT) are given in the diagram below.

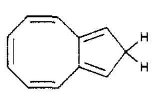


Addition of HMPT to DME or MTHF not only prolonged the lifetime of $1^{\bullet-}$ and enabled one to study its ESR spectrum (see above) but also changed the course of the reaction leading to secondary products. When DME/HMPT or MTHF/HMPT solutions exhibiting the spectrum of $1^{\bullet-}$ were brought into a renewed contact with the potassium metal, this spectrum was superseded by that of a hitherto unknown persistent species (g = 2.0027 ± 0.0001). Figure 3 shows the ESR spectrum of the new species, together with its computer-simulation and the corresponding proton ENDOR signals. The coupling constants are as follows: 0.586 ± 0.004, 0.509 ± 0.004, 0.328 ± 0.003, and 0.005 ± 0.001 mT, each from two equivalent protons, 0.097 ± 0.001 mT from a single proton, and 0.023 ± 0.001 mT from two equivalent ^{39}K nuclei of the two counterions. A secondary paramagnetic species, obtained by an analogous procedure from 2-D-**1**, was characterized by the same hyperfine data, except for a deuteron coupling constant of 0.015 ± 0.001 mT replacing the one-proton value of 0.097 mT.

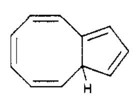
ESR and ENDOR spectra identical with those in Figure 3 were observed when a mixture of the three isomeric bicyclo[6.3.0]undecapentaenes, **5**-H(1), **5**-H(2), and **5**-H(3a), was subjected to a prolonged contact with potassium metal under similar conditions.



5-H(1)

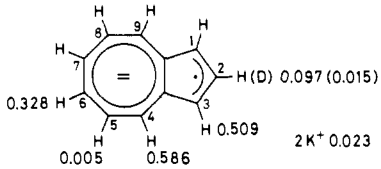


5-H(2)



5-H(3a)

This finding leaves no doubt that the paramagnetic species in question is the radical dianion $5^{\bullet 2-}$. The structure $5^{\bullet 2-}$ is also supported by MO models[20] which afford reliable assignments of the coupling constants to protons in individual positions, as indicated in the diagram below (values in mT).



Discussion

The π-Perimeter Model. Figure 4 depicts the degenerate lowest antibonding MO's of the 10-membered π-perimeter. They are classified as symmetric (ψ_S) and antisymmetric (ψ_A) with respect to a vertical mirror plane (m) passing through two opposite centers. The shapes of the perimeter in Figure 4 are adapted to the carbon frameworks of the cyclic π-systems in the isomeric bridged [10]annulenes 1 and 2. It has previously been pointed out[13] that perturbations by the bridging group which are relevant to the removal of the degeneracies in the frontier perimeter MO's can be considered as arising from homoconjugative, inductive, and hyperconjugative interactions. In the following, the effect of these

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(18) Bauld, N. L.; Brown, M. S. *J. Am. Chem. Soc.* **1967**, *89*, 5417.

(19) Gerson, F.; Huber, W.; Müllen, K. *Helv. Chim. Acta* **1981**, *64*, 2766.

(20) The π-spin populations ρ_μ calculated for the proton-bearing π-centers μ in $5^{\bullet 2-}$ by the McLachlan procedure ($\lambda = 1.2$)[21] are as follows: μ = 1,3; 2; 4,9; 5,8; 6,7; and ρ_μ = +0.172; −0.045; +0.238; +0.008; +0.118, respectively.

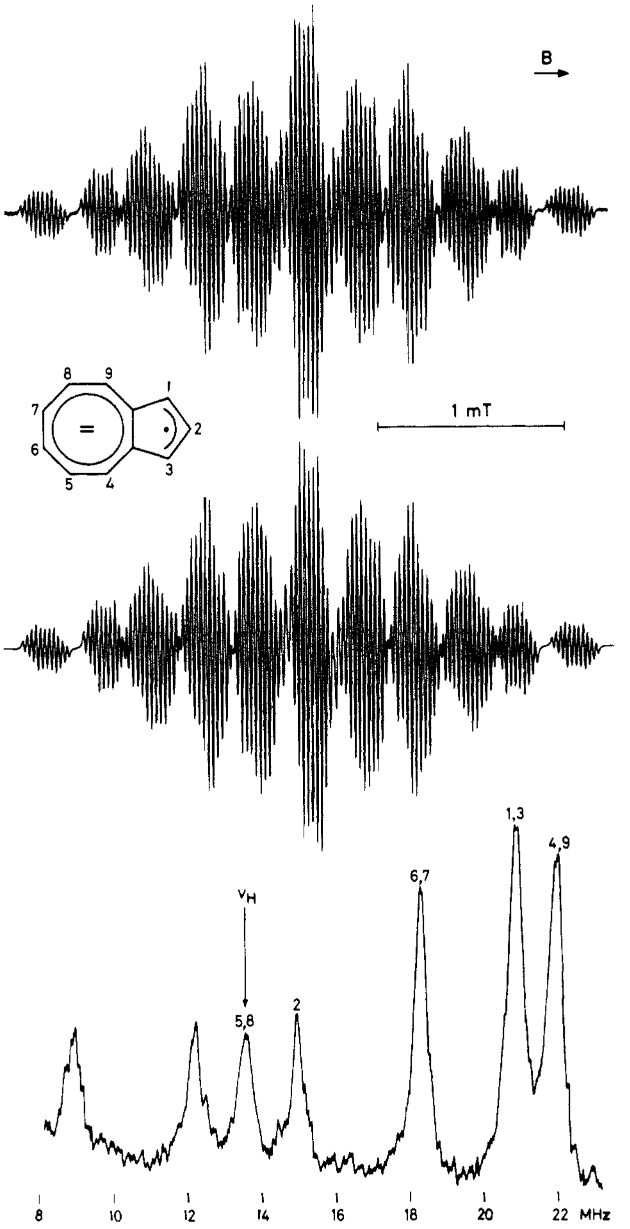

Figure 3. Top: ESR spectrum of $5^{\bullet 2-}$. Solvent, DME/HMPT (5:1), counterions, K$^+$; temperature, 193 K. Middle: computer-simulation. Coupling constants, see text; line shape, Lorentzian; line width, 0.015 mT. Bottom: proton ENDOR spectrum of $5^{\bullet 2-}$. Experimental conditions as for the ESR spectrum. ν_H = frequency of the free proton. The numbers above the ENDOR signals denote the positions of the protons assigned to these signals.

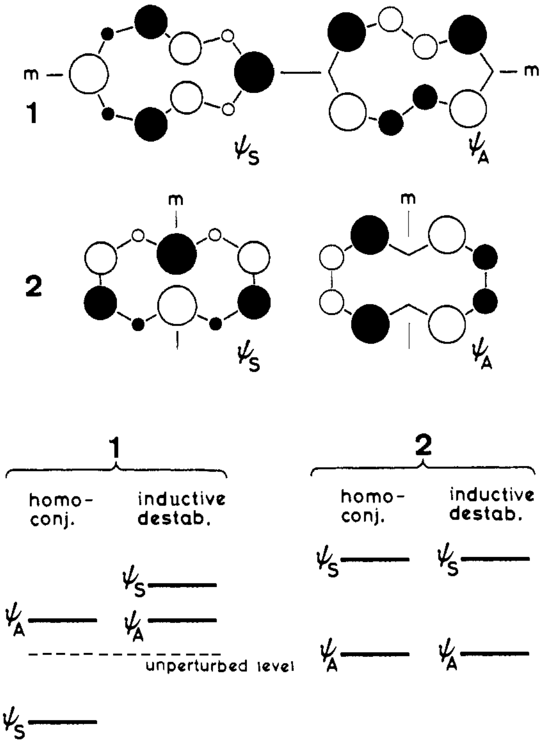

Figure 4. Top: schematic representations of the degenerate lowest antibonding MO's of the 10-membered π-perimeter. The areas of the circles are proportional to the squares of the LCAO coefficients. Filled and blank areas symbolize opposite signs of these coefficients. Bottom: removal of the degeneracy by the "separate" effects of homoconjugation and inductive destabilization in **1** and **2** (not to scale).

interactions on the energies of ψ_S and ψ_A will be discussed for both **1** and **2** in terms of the first order perturbation treatment.

Homoconjugative interaction is proportional to the *product* of the LCAO coefficients at the two bridged centers. Thus, in **1**, ψ_S should be substantially stabilized (relatively large coefficients of the same sign), whereas ψ_A is expected to be weakly destabilized (smaller coefficients of opposite sign). In **2**, on the other hand, only ψ_S should be subject to homoconjugation, since ψ_A exhibits a node through the bridged centers; the energy of ψ_S is predicted to be strongly raised in this case (very large coefficients of opposite sign).

Inductive destabilization by the methano bridging group depends on the *squares* of the LCAO coefficients at the bridged centers. In **1**, it should, therefore, raise the energy of ψ_S to a larger extent than that of ψ_A. As for **2**, the inductive perturbation is expected to act on the two MO's in the same direction as homoconjugation by strongly destabilizing ψ_S without affecting ψ_A.

Hyperconjugation cannot be effective for ψ_A in **1** and for ψ_S in **2**, as these MO's have a nodal plane passing through the methano bridging group. Moreover, it should be negligible for ψ_A in **2**, considering the vanishing LCAO coefficients at the bridged centers. Only ψ_S in **1** is qualified for a substantial hyperconjugative interaction with a bridging group σ-orbital of an appropriate symmetry, and it is undoubtedly this interaction which leads to a marked spin transfer onto the 9-exo-hydrogen atom in $1^{\bullet-}$ (see following section). However, the effect of hyperconjugation on the energy of an antibonding π-MO such as ψ_S is difficult to predict in regard to both direction and magnitude. One may reasonably assume that it is small relative to those of homoconjugative and inductive perturbations.[22] In Figure 4, where the predicted effects of the "separate" perturbations on the energies of ψ_S and ψ_A are schematically summarized for **1** and **2**, hyperconjugation has, therefore, been left out, and only homoconjugation and inductive destabilization are considered.

It is evident that the SOMO in $2^{\bullet-}$ must resemble ψ_A, since both perturbations destabilize ψ_S. This conclusion has been unequivocally confirmed by experiment.[10a,12] The situation is less clear for $1^{\bullet-}$, as the predicted energy sequence of ψ_S and ψ_A is different for the "separate" perturbations. Whereas homoconjugation favors ψ_S, the inductive destabilization makes ψ_A the preferred MO. However, one can argue that the inductive destabilization of ψ_S should be outweighed by homoconjugative stabilization which in **1** is particularly promoted by the bending of the perimeter (see Introduction). By contrast, homoconjugation and inductive perturbation would reinforce each other in raising the energy of ψ_A. As a result, one is justified to expect that ψ_S *will lie below* ψ_A, i.e., *the energetic sequence of the two MO's in* **1** *will be determined by homoconjugation rather than by inductive perturbation.* It is shown in the following section that this expectation is fully borne out by experiment which unequivocally establishes that *the SOMO in* $1^{\bullet-}$ *correlates with the perimeter MO* ψ_S.

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[21] McLachlan, A. D. *Mol. Phys.* **1960**, *3*, 233.

[22] For an antibonding π-MO (π^*), interactions with both bonding (σ) and antibonding (σ^*) orbitals of an alkyl group have to be taken into account. Since the interaction with the σ-orbitals raises the energy of the π^*-MO and that with the σ^*-counterparts lowers it, the net effect is likely to be small.

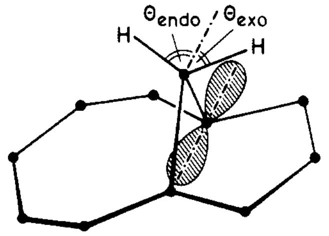
Symmetry of the SOMO in 1$^{\bullet-}$ and Assignments of the Coupling Constants. The half-wave reduction potential of **1**, which can be estimated as −1.94 ± 0.01 V from the chemically irreversible wave at −1.97 V,[23] is distinctly less negative than the $E_{1/2}$ value of −2.21 V observed for **2**. The LUMO in **1** must thus lie energetically *lower* than the corresponding ψ_A-like MO in **2**.[10a,12] As is evident from the energy diagram in Figure 4, this finding requires that the LUMO in **1** should resemble ψ_S which is stabilized relative to ψ_A by homoconjugation. A ψ_S-like LUMO in **1** is also consistent with the $E_{1/2}$ value of −1.63 V measured for azulene (**3**),[24] since the LUMO in **3** undoubtedly correlates with ψ_S[9] of which the energy is further lowered on going from homoconjugation in **1** to a full conjugation in **3**.

Last but not least, the hyperfine data for **1**$^{\bullet-}$ tally with a SOMO exhibiting the nodal properties of ψ_S. Most relevant in this respect are the coupling constants of 1.342, 0.685, 0.432, and 0.045 mT, which were observed for the single protons in **1**$^{\bullet-}$, i.e., for those at the π-centers 2 and 6 (α-protons) and at the bridging carbon atom 9 (β-protons).[25] The large values of three out of four coupling constants in question are fully compatible with a ψ_S-like SOMO, whereas they rule out a single occupancy of an MO resembling ψ_A which has a nodal plane (m) passing through the centers 2 and 6 and the CH_2 group (Figure 4).

The largest coupling constants of 1.342 mT, which is the most prominent hyperfine feature of **1**$^{\bullet-}$, have been assigned by deuteration (see Results) to the β-proton situated above the "homocyclopentadienyl" moiety (9-exo-position). Values of this size are diagnostic of a hyperconjugative spin transfer from a π-type SOMO to a σ-orbital in a CH_2 or CH group which is simultaneously linked to two π-centers bearing large LCAO coefficients of the same sign.[26] Obviously, this situation exists in **1**$^{\bullet-}$ when the SOMO resembles ψ_S. The coupling constant, $a_H{}^{\beta}$, of a β-proton in the methano bridging group can then be expressed by the relationship[27]

$$a_H{}^{\beta} = B(c_{S3a} + c_{S8a})^2 \cos^2 \theta \qquad (1)$$

where $c_{S3a} = c_{S8a} = 0.362$ are the LCAO coefficients for the MO ψ_S at the bridged centers 3a and 8a, and where θ is the dihedral angle between the pertinent C–H$^{\beta}$ bond and the 2p axes at each of these centers. Taking $B = +4.0$ to $+4.5$ mT as the proportionality factor appropriate for radical anions[28] and setting $a_H{}^{\beta} = a_{H9\text{-exo}} = 1.342$ mT, one obtains $\theta_{exo} \approx 40°$. This result is compatible with the geometry of **1**, as indicated by molecular models.



The corresponding angle θ_{endo} is ca. 80°, since θ_{exo} and θ_{endo} must add up to 120°. By using this value of θ_{endo} in eq 1, one predicts that the coupling constant, $a_H{}^{\beta} = a_{H9\text{-endo}}$, of the β-proton situated above the "homocycloheptatrienyl" moiety (9-endo-position) should be less than 0.1 mT. An assignment of 0.045 mT to this proton thus is justified.

The two remaining one-proton coupling constants of 0.685 and 0.432 mT must arise from the α-protons at the centers 2 and 6. Since the latter value has been assigned by deuteration (see Results) to the proton at the center 2, the former is left for that at the center 6. As will be shown below, both experimental coupling constants are in essential agreement with their theoretical counterparts.

For lack of spectroscopic evidence, assignments of 0.367, 0.328, and 0.091 mT to pairs of equivalent protons in **1**$^{\bullet-}$ must be fully based on MO models. To this aim, π-spin populations ρ_μ at centers μ were calculated by the McLachlan procedure ($\lambda = 1.2$)[21] for the SOMO ψ_S in the radical anion of a hypothetical planar [10]annulene. The dominant effect of a homoconjugative perturbation was introduced through an additional bond parameter $\beta_{3a8a} = k\beta$ for a transannular interaction between the bridged centers 3a and 8a. Variation of k from 0 to 1 thus represents an increase of such interaction from none in an unperturbed [10]-annulene to full conjugation as realized in **3**. The π-spin populations ρ_μ were converted into the coupling constants, $a_{H_\mu}{}^{\alpha}$, of the α-protons at the centers μ with use of the McConnell relationship[30]

$$a_{H_\mu}{}^{\alpha} = Q\rho_\mu \qquad (2)$$

where the proportionality factor Q was set equal to −2.25 mT.[31] The $a_{H_\mu}{}^{\alpha}$ values thus obtained are listed in Table I, along with corresponding hyperfine data for **1**$^{\bullet-}$ and **3**$^{\bullet-}$. As has been noticed in an earlier study,[32] eq 2 holds less exactly for **3**$^{\bullet-}$ than for the radical ions of benzenoid hydrocarbons, because of the failing constancy of the proportionality factor Q. Nevertheless, the proton hyperfine data for **3**$^{\bullet-}$ are fairly well reproduced by theory when $0.75 \leq k \leq 1.0$ and so are the two coupling constants of the single α-protons in **1**$^{\bullet-}$ when $0.25 \leq k \leq 0.50$ (Table I). It is, therefore, reasonable to assign the largest two-proton coupling constant for **1**$^{\bullet-}$, 0.367 mT, to the pair of protons at the centers 4 and 8 which exhibits a calculated $|a_{H_\mu}{}^{\alpha}|$ value of comparable size. More problematic are assignments of the remaining two-proton coupling constants, 0.328 and 0.091 mT, as the larger one has no appropriate counterpart in the MO model (Table I). Although its assignment to the protons at the centers 5 and 7, leaving the smaller value for those at 1 and 3, appears more attractive, an alternative choice cannot be excluded. The striking discrepancy between theory and experiment in the case of 0.328 mT is too large to be attributed to a deficiency of the McLachlan procedure but must be due to deviations of the 10-membered perimeter from planarity (see next section).

Effect of Nonplanarity. Bending of a π-system out of planarity can considerably alter the α-proton coupling constants, $a_{H_\mu}{}^{\alpha}$, relative to the values expected for a corresponding planar radical.[10,14] This is because π–σ spin *delocalization* then becomes superimposed on π–σ spin *polarization* which accounts for $a_{H_\mu}{}^{\alpha}$ values in a planar π-radical, according to eq 2. Depending on the relative signs of the contributions to $a_{H_\mu}{}^{\alpha}$ from the two mechanisms of spin transfer, deviations of the π-system from planarity lead to an increase or a decrease in the observed (absolute) values of $a_{H_\mu}{}^{\alpha}$. For **2**$^{\bullet-}$, e.g., where the π-spin populations at the proton-bearing centers μ are throughout positive, the contributions to $a_{H_\mu}{}^{\alpha}$ by spin polarization and delocalization have negative and positive signs, respectively. As a result, the $|a_{H_\mu}{}^{\alpha}|$ values are markedly smaller than those predicted for a planar π-radical anion with a similar spin distribution.[10] A suitable reference species is the radical anion of naphthalene (**6**), since the SOMO in **6**$^{\bullet-}$, like that of **2**$^{\bullet-}$, can be represented by an essentially unperturbed MO ψ_A of the 10-membered perimeter. The two coupling constants, 0.271 and 0.010 mT, each for a set of four equivalent α-protons in **2**$^{\bullet-}$ are drastically reduced relative

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(23) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

(24) Gerson, F.; Lopez, J.; Metzger, A.; Jutz, Ch. *Helv. Chim. Acta* **1980**, *63*, 2135.

(25) In ESR spectroscopy, protons separated from a π-center by 0,1,2,... sp^3-hybridized carbon atoms are denoted α, β, γ ...

(26) For some pertinent examples in the series of bridged annulenes, see: Elschenbroich, Ch.; Gerson, F.; Boekelheide, V. *Helv. Chim. Acta* **1975**, *58*, 1245. Huber, W. *Helv. Chim. Acta* **1984**, *67*, 1825. Gerson, F.; Huber, W. *Angew. Chem.* **1985**, *97*, 496; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 495. See, also: ref 13.

(27) Whiffen, D. H. *Mol. Phys.* **1963**, *6*, 223.

(28) $|B|$ = 4.0 mT is suggested by Russell, G. A. In *Radical Ions*; Kaiser, E. T., Kevan, L., Eds.; Interscience Publishers: New York, 1967; Chapter 3. $|B|$ = 4.5 mT ≈ 2 × 2.24 mT is derived from an ESR study on the radical anions of dimethyl-substituted naphthalenes.[29]

(29) Gerson, F.; Weidmann, B.; Heilbronner, E. *Helv. Chim. Acta* **1964**, *47*, 1951.

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

(31) $|Q|$ = 2.25 mT is the total width in the ESR spectrum of benzene radical anion. This value is also close to the average proportionality factor which is obtained on applying eq 2 to **3**$^{\bullet-}$.[32]

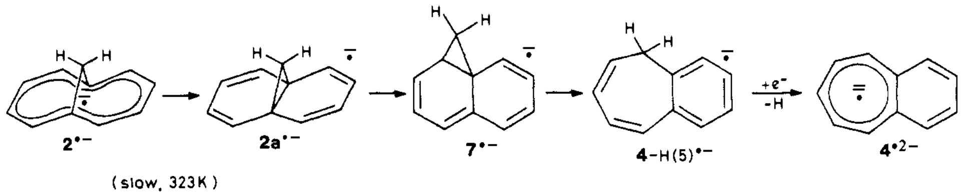
(32) Bernal, I.; Rieger, P. H.; Fraenkel, G. K. *J. Chem. Phys.* **1962**, *37*, 1489.

Table I. Calculated and Observed α-Proton Coupling Constants, $a_{H_\mu}{}^{\alpha}$ in mT, for the Radical Anions of Homoazulene (**1**) and Azulene (**3**)

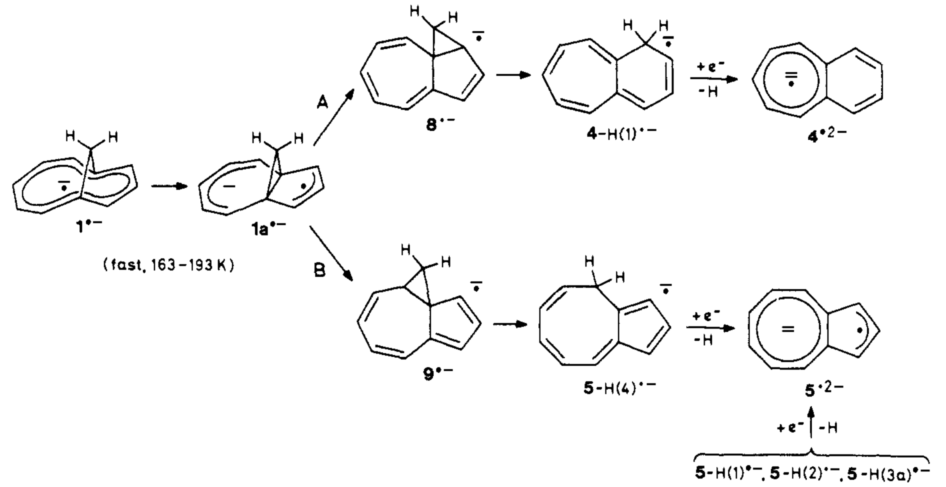
	$a_{H_\mu}{}^{\alpha}$ calculated[a]					$\lvert a_{H_\mu}{}^{\alpha}\rvert$ observed	
μ	$k = 0$	0.25	0.50	0.75	1.00	$\mathbf{1}^{\bullet-}$[b]	$\mathbf{3}^{\bullet-}$[c]
1,3	+0.084	+0.083	+0.077	+0.067	+0.056	0.091	0.027
2	−0.602	−0.493	−0.393	−0.310	−0.245	0.432	0.389
4,8	−0.347	−0.441	−0.534	−0.616	−0.683	0.367	0.613
5,7	+0.085	+0.112	+0.140	+0.167	+0.191	0.328	0.121
6	−0.609	−0.679	−0.746	−0.801	−0.844	0.685	0.873

[a] See text. [b] This work. [c] Reference 24.

Scheme I



Scheme II



to the corresponding values, 0.495 and 0.183 mT,[29] for $\mathbf{6}^{\bullet-}$.

Interestingly, the $\lvert a_{H_\mu}{}^{\alpha}\rvert$ values observed for $\mathbf{1}^{\bullet-}$ can, with one exception (0.328 mT), be reasonably fitted into the MO model of a planar [10]annulene (Table I). There is even some resemblance between the α-proton hyperfine data for $\mathbf{1}^{\bullet-}$ and $\mathbf{3}^{\bullet-}$ although the perimeter MO ψ_S, which correlates with the SOMO's in both $\mathbf{1}^{\bullet-}$ and $\mathbf{3}^{\bullet-}$, is appreciably modified on promoting homoconjugation in **1** to full conjugative interaction in **3**. The finding that the α-proton coupling constants for $\mathbf{1}^{\bullet-}$ are apparently less affected by deviations of the π-system from planarity than the analogous values for $\mathbf{2}^{\bullet-}$ is rather surprising, since the perimeter should be even more strongly bent in the former than in the latter radical anion.[33] Thus, the response of the $a_{H_\mu}{}^{\alpha}$ values to the nonplanarity of the cyclic π-system must, in general, be weaker for $\mathbf{1}^{\bullet-}$ than for $\mathbf{2}^{\bullet-}$, a behavior which should be traced to different nodal properties of the SOMO's in the two radical anions. In $\mathbf{1}^{\bullet-}$, by contrast to $\mathbf{2}^{\bullet-}$, these properties give rise to alternately positive and negative π-spin populations ρ_μ at the proton-bearing centers μ, so that the contributions to $a_{H_\mu}{}^{\alpha}$ due to nonplanarity of the π-system are likely to partially cancel because of opposite signs. Some enhancement in $\lvert a_{H_\mu}{}^{\alpha}\rvert$, relative to the values predicted for a planar π-radical anion, may be met with the protons at the centers $\mu = 1$ and 3 and/or 5 and 7 which exhibit negative π-spin populations, since in this case the contributions to $a_{H_\mu}{}^{\alpha}$ by π–σ spin delocalization can have the same (positive) sign as those arising from π–σ spin polarization. Such an enhancement would provide a rationalization of the unexpectedly large size, 0.328 mT, of the coupling constant assigned to the α-protons at the centers 5 and 7 (with 1 and 3 as a viable alternative).

Rearrangements. Prior to discussing the secondary products formed upon exhaustive reduction of **1**, it is advisable to recall the corresponding results for the isomeric compound **2**. The primary reduction product, the very persistent radical anion $\mathbf{2}^{\bullet-}$, rearranges to the bicyclo[5.4.0]undeca-1,3,5,7,9-pentaenyl (benzotropyl, **4**) π-system, only after being exposed for several hours to the potassium mirror, preferably at higher temperatures (323 K).[11] Scheme I presents the sequence of reaction steps postulated for the conversion of $\mathbf{2}^{\bullet-}$ into the radical dianion $\mathbf{4}^{\bullet 2-}$ which was identified as the final paramagnetic product. The intermediately formed radical anions $\mathbf{2a}^{\bullet-}$ (a valence isomer of $\mathbf{2}^{\bullet-}$), $\mathbf{7}^{\bullet-}$, and $\mathbf{4}$-H(5)$^{\bullet-}$ are too short-lived under the applied experimental conditions to be characterized by ESR spectroscopy. Owing to the C_{2v} symmetry of $\mathbf{2}^{\bullet-}$, rearrangement to only one π-system is observed.

An analogous sequence of reaction steps, as depicted in Scheme II, is suggested for the rearrangements of $\mathbf{1}^{\bullet-}$ which are distinguished from that of $\mathbf{2}^{\bullet-}$ by two conspicuous features: (i) the higher reactivity (lesser persistence) which makes the conversion of $\mathbf{1}^{\bullet-}$ into secondary products proceed more rapidly and at lower temperatures (163–193 K) and (ii) the C_s symmetry which paves two separate reaction pathways, A and B, leading to two different rearranged π-systems. As stated in the Results, the pathway A terminating in $\mathbf{4}^{\bullet 2-}$ is followed when the solvents DME and MTHF are used without an admixture of HMPT. On the other hand, in the presence of HMPT, the course of reaction is diverted to the pathway B which leads to the radical dianion of bicyclo[6.3.0]undeca-1,3,5,7,9-pentaenyl (**5**), an isomer of $\mathbf{4}^{\bullet 2-}$, as the final paramagnetic product. Again, the radical anions proposed as intermediates in pathways A and B must have only a transient

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[33] It has quite recently been suggested[34] that π-orbital alignment in **1** and **2** can be improved by rehybridization of the carbon atoms. As a result, the cyclic π-systems in **1** and **2** would achieve a comparable degree of planarity.

existence in solutions contacting the potassium mirror, since their ESR spectra are not observed. This statement refers to **1a**$^{\bullet-}$ (a valence isomer of **1**$^{\bullet-}$) as well as to **8**$^{\bullet-}$ and **4**-H(1)$^{\bullet-}$ in pathway A or to **9**$^{\bullet-}$ and **5**-H(4)$^{\bullet-}$ in pathway B. In particular, **5**-H(4)$^{\bullet-}$ should readily convert into **5**$^{\bullet 2-}$, as do the isomeric radical anions **5**-H(1)$^{\bullet-}$, **5**-H(2)$^{\bullet-}$, and **5**-H(3a)$^{\bullet-}$ which undoubtedly are the primary reduction products of the reaction starting from a mixture of corresponding neutral bicyclo[6.3.0]undecatetraenes and yielding **5**$^{\bullet 2-}$ as a single final product (see Results). It is noteworthy that a thermal rearrangement of the neutral **1** into a variety of products can be accounted for by a pathway involving the intermediates **1a**, **9**, and **5**-H(4) (a known compound[35]), whereas an alternative route via **1a**, **8**, and **4**-H(1) has to be disregarded.[36] This result may be combined with the present finding that addition of HMPT to DME or MTHF changes the course of reaction from pathway A to B. Since solvation by HMPT weakens the association between a hydrocarbon anion and its alkali metal counterion, such a change is presumably due to a loosening of ion pairing. The available evidence thus enables one to suggest that the rearrangement of **1** to the π-system of **5** is preferred for a neutral compound or a nonassociated radical anion, whereas pairing of **1**$^{\bullet-}$ and/or **1a**$^{\bullet-}$ with the counterion K$^+$ favors the rearrangement to the π-system of **4**.

Concluding Remark. The present studies on the radical anion of homoazulene (**1**) stress the *important role of homoconjugation* in determining the electronic structure of the compound **1**. In accord with the prediction of the simple perturbation treatment applied here to the degenerate lowest antibonding MO's of the 10-membered perimeter, the LUMO of **1** is *symmetric* with respect to the mirror plane passing through two opposite π-centers, and it thus correlates with the corresponding MO of azulene (**3**). When an analogous treatment is used for the degenerate highest bonding perimeter MO's, an energy sequence closely resembling that depicted in Figure 4 for **1** is obtained. This means that again, due to homoconjugation, the symmetric MO should be stabilized relative to its antisymmetric counterpart. It is, therefore, an *antisymmetric* MO which is expected to become the HOMO of **1** and thus to correlate with the corresponding MO of **3**.[9] The similar nodal properties of both frontier orbitals in **1** and **3** provide a theoretical basis for rationalizing the electronic features common to the two compounds such as adherence of the long-wave absorption band to Plattner's rules. These common features fully justify the name of homoazulene given to the novel bridged [10]annulene **1**.

Experimental Section

Materials. Homoazulene (1). The synthesis of **1** has been described previously.[2b,4]

2-Deuteriohomoazulene (2-D-1). Deuterium was introduced into the 2-position of homoazulene at an intermediate stage in the synthesis. Thus, 180 mg (1.12 mmol) of tricyclo[5.3.1.0]undeca-3,5-dien-8-one[4] in 4 mL of tetrahydrofuran (THF) was stirred at room temperature for 15 h with 1.5 mL of 0.1 M NaOD in D_2O. After removal of THF under reduced pressure, the remaining mixture was extracted with ether. This solution was dried over magnesium sulfate, and the ether was removed under reduced pressure yielding 175 mg (96% recovery) of a nearly colorless oil. Analysis by NMR indicated >90% exchange at C(9). This material was carried on to 2-D-**1** by the procedure used previously.[4]

9-*exo*-Deuteriohomoazulene (9-exo-D-1). Under a nitrogen atmosphere, 106 mg (0.745 mmol) of homoazulene (**1**) in 2 mL of dry THF was added rapidly via syringe with stirring to a fivefold excess of lithium diisopropylamide (3.73 mmol) in 8 mL of dry THF at −78 °C. The resulting dark red solution was stirred for 3.5 min at −78 °C, and then 2.5 mL of D_2O (99.9%) was added all at once. The yellow-orange solution thus obtained was allowed to warm to room temperature. Concentration under reduced pressure at this temperature gave an orange solution which was extracted with 25 mL of *n*-pentane. The pentane layer was washed with 2 × 30 mL of saturated aqueous sodium chloride, dried over magnesium sulfate, and concentrated under reduced pressure at room temperature to yield an orange oil. Preparative layer chromatography on alumina with pentane as the eluant gave 24 mg (23%) of 9-exo-D-**1**. Analysis by NMR showed >90% incorporation of deuterium at the 9-exo position. The sterochemistry of the product follows from the finding that the long-range W-coupling (1.6 Hz) between the second hydrogen (9-endo) of the CH_2-bridging group and the hydrogens in the 1- and 3-positions has been preserved.

Bicyclo[6.3.0]undecapentaenes 5-H(1), 5-H(2), and 5-H(3a). A mixture of these three isomers, with **5**-H(1) as the major product, was obtained by irradiation of diazocyclopentadiene in benzene, according to a procedure described in the literature.[37]

Preparation of the Radical Anions. Because of instability of the neat homoazulene (bright orange oil at room temperature),[4] samples of **1**, 2-D-**1**, and 9-exo-D-**1**, synthesized in the Reno laboratory, had to be transferred to Basel as diluted solutions in pentane. In the Basel laboratory, pentane was removed under reduced pressure, and it was replaced by a solvent appropriate for the conversion of the neutral compound into its radical anion.

Instrumental. The equipment for the cyclic voltammetry included a potentiostat/galvanostat Model 173 and universal programmer 175, both of Princeton Applied Research (PAR). The spectral apparatus consisted of a Varian-ESR-E9 spectrometer with an attached Varian-ENDOR-1700 system.

Acknowledgment. This work was supported by the National Science Foundations of Switzerland and U.S.A.

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Double Nitrogen Inversion in Sesquibicyclic Hydrazines and Their Cation Radicals

Stephen F. Nelsen,* Timothy B. Frigo, Yaesil Kim, and James A. Thompson-Colón

Contribution from the S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received May 20, 1986

Abstract: The barrier to double nitrogen inversion in **4** (measured by observing the rate of bridgehead equilibration in **4**-d_6 by ^{1}H NMR) is 27.0 kcal/mol at 80 °C, substantially higher than the 10.3 kcal/mol at −55 °C observed for **2** (by ^{13}C DNMR). The barrier to double nitrogen inversion in **4**$^{\bullet+}$ (determined by dynamic ESR measurements on **4**-$d_{12}{}^{\bullet+}$) is 4.6 kcal/mol at −85 °C. The effects of ring homologation on the amount of bend at nitrogen in sesquibicyclic hydrazines and their cation radicals as indicated by conformational and spectral measurements is discussed, and it is shown that AM1 calculations are able to predict the observed behavior rather well.

1,2-Dialkyl-1,2,3,6-tetrahydropyridazines, A, readily undergo thermal retro-Diels–Alder cleavage to dienes and azo compounds[1] (reaction 1). Conditions which allow the reverse reaction, Diels–Alder synthesis of A (Reaction 2), have only recently been