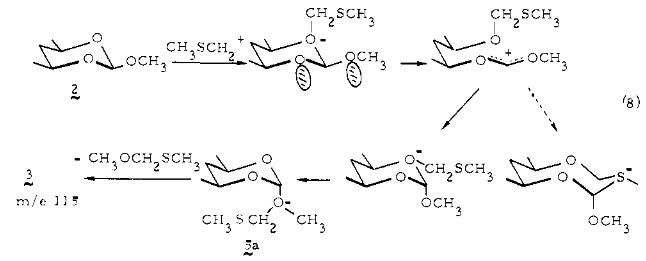
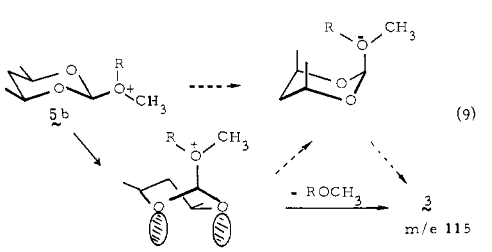


(8)

and, in the case of R = CH_3SCH_2, a more likely process would be cyclization by C-S bond formation to give a sulfonium ion, contrary to observation.

A further point to consider is whether the energy of ion-molecule association in the initial encounter (i.e., the well depth of the first minimum in Figure 4) is sufficient to fuel ring inversion to higher energy conformations. The association energy may be substantial (~20 kcal mol^{-1}).[26] If ring inversion occurs, the axial C-O bond would almost certainly dissociate spontaneously. However, it is not necessary for **5b** to convert to the all-axial chair conformation in order to lose the exocyclic methoxyl group. Conversion to a boat form would also situate the interacting orbitals on the ring oxygens antiperiplanar to the exocyclic C-O bond, and this would presumably lead to facile dissociation (eq 9).



(9)

The present system of conformationally biased 1,3-dioxanes **1** and **2** cannot then provide a definitive test of stereoelectronic control in the gas phase because of potentially accessible twist-boat forms. In the continuation of this work, it will be necessary to employ systems that have fixed conformations that exclude even boat-chair interconversions. Regardless of interpretation, the interesting fact remains that the greater propensity for ionic cleavage of the axial methoxyl in **1** relative to the equatorial methoxyl in **2** in condensed phase is not evident in the gas phase.

Acknowledgment. We gratefully acknowledge the support of this work through Grant no. CHE 7807993 awarded by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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(26) J. L. Beauchamp in "Interactions Between Ions and Molecules", P. Ausloos, Ed., Plenum Press, New York, 1975.

Alkyl Group Stabilization of Monoolefin Radical Cations. An ESR, ENDOR, and Cyclic Voltammetry Study

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Abstract: The ESR spectrum of the radical cation of adamantylideneadamantane (**1**) exhibits proton coupling constants of 0.605 (4, δ-H), 0.327 (8 equatorial, γ-H), 0.058 (4 H), 0.047 (8 axial, γ-H), and 0.012 mT (4 H). The indicated assignment was secured by the studies of the δ-d_2 (**2a**/**2b**) and equatorial-γ-d_1 (**3**) species. For the radical cation of bis(bicyclo[3.3.1]non-9-ylidene) (**4**), the proton coupling constants determined from its ESR spectrum are 0.370 (8, γ-H), 0.320 (4 H), 0.105 (4 H), and 0.055 mT (8, γ-H), while the ENDOR measurements on the radical cation of 9,9′-bis(9-azabicyclo[3.3.1]nonane) (**5**) yield 0.160 (4 H), 0.128 (8, γ-H), 0.099 (4 H), 0.059 (8, γ-H), and 0.027 mT (4 H). Cyclic voltammetry (CV) gives $E^{\circ\prime}$ values (vs. SCE; solvent CH_3CN) of 1.45 V for **1**, 1.49 V for **4**, 1.61 V for 4(e)-chloroadamantylideneadamantane (**8**), and 1.35 V for bis(homoadamantane) (**9**). The implication of these hyperfine and CV data on the electronic structure and physicochemical properties of the pertinent compounds and their radical cations is discussed.

The lability of C-H bonds at carbon atoms directly attached to a π center bearing a high spin population leads to a short lifetime of the radical and makes the study of such a radical difficult. It has been shown that alkyl groups which force the pertinent C-H bonds to lie perpendicular to the axis of the spin-bearing $2p_z$ AO confer substantial kinetic stability (persistence) on a radical. Paramagnetic species exhibiting this structural feature have been called "Bredt's rule protected". Relevant examples are secondary nitroxides[2] and hydrazine radical cations,[3] both of which may be isolated, as well as the long-lived hydrazyl and α-amino radicals,[3,4] and some trialkylamine and dialkylchloroamine radical cations.[3] It has recently been found that Bredt's rule protection also contributes to the persistence of the adamantylideneadamantane (**1**) radical cation.[5]

This paper deals with ESR studies on the radical cations of **1** and its deuterio derivatives **2a**/**2b** and **3**, together with those of the bicyclo[3.3.1]nonane analogue **4** and the structurally related hydrazine **5** and its diketo derivative **6**. In the case of **5**, use of ENDOR spectroscopy was essential for the determination of the proton hyperfine data. The notation employed for the protons is specified in the formulas by indicating one hydrogen atom for each set of equivalent protons; the numbering scheme of the carbon

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(1) (a) Universität Basel. (b) University of Wisconsin.

(2) Dupeyre, R.M.; Rassat, A. *J. Am. Chem. Soc.* **1966**, *88*, 3180.

(3) (a) Nelsen, S. F.; Kessel, C. R. *J. Am. Chem. Soc.* **1977**, *99*, 2392. (b) Nelsen, S. F.; Kessel, C. R. *J. Chem. Soc., Chem. Commun.* **1977**, 490. (c) Nelsen, S. F.; Kessel, C. R.; Brien, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 702.

(4) Nelsen, S. F.; Landis, R. T., II *J. Am. Chem. Soc.* **1974**, *96*, 1788.

(5) Nelsen, S. F.;, Kessel, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 2503.

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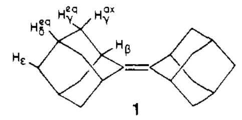
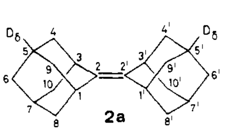
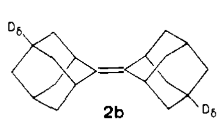


1



2a



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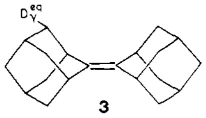

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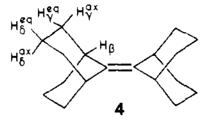
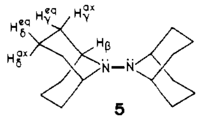
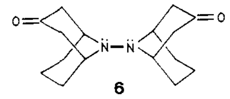


4

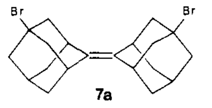


5

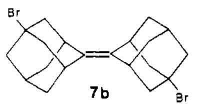


6

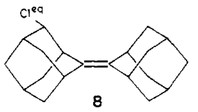
atoms is shown in formula **2a**. Results obtained by cyclic voltammetry (CV) for **1**, **4**, halogenated adamantylideneadamantanes **7a**/**7b** and **8**, and bis(homoadamantane) (**9**) are also reported.



7a



7b



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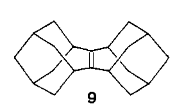

9

Experimental Section

The spectral apparatus consisted of a Varian ENDOR-1700 system attached to a Varian ESR-E9 instrument. The experimental error in the proton coupling constants is estimated as 0.5% for $1^{+\cdot}$, 1% for $2a^{+\cdot}/2b^{+\cdot}$, $3^{+\cdot}$ and $5^{+\cdot}$, and 2% for $4^{+\cdot}$. The ^{14}N-coupling constants for $5^{+\cdot}$ and $6^{+\cdot}$ and the *g* factors were subjected to an uncertainty of ±0.01 mT and ±0.0001, respectively.

The CV experiments were conducted as previously described.[3c]

Adamantylideneadamantane (1) was prepared by the method of Schaap and Faler.[6]

5,5'/7'-Dibromoadamantanone Azine. A solution of 0.29 g (5.51 mmol) of 99% hydrazine hydrate in 3 mL of *tert*-butyl alcohol was added dropwise over 8 min to a refluxing, stirred solution of 1.74 g (7.59 mmol) of 5-bromo-2-adamantanone[7] in 13 mL of *tert*-butyl alcohol, the mixture was refluxed for 20 h and allowed to stand at room temperature for the same period of time. After removal of *tert*-butyl alcohol under reduced pressure, 45 mL of water was added and the product was extracted into ether, dried over magnesium sulfate, and concentrated to give 1.53 g (91%) of crude azine, mp 171–176 °C, which was carried on to the next step. Recrystallization from hexane gave the following: mp 175–179 °C;[8] ^1H NMR $\delta(CDCl_3)$ 1.70–2.10 (m, 8 H), 2.25 (m, 2 H), 2.3–2.7 (m, 12 H), 2.78 (m, 2 H), 3.50 (m, 2 H); IR (cm^{-1}, CCl_4) 2900, 2840, 1635, 1440.

5-Bromoadamantanespiro-2'-(1',3',4'-thiadiazolidine)-5'-spiro-5''/7''-bromoadamantane. Hydrogen sulfide was bubbled into a stirred mixture of 3.37 g (7.42 mmol) of the dibromoazine in 30 mL of 3:1 benzene/acetone, and the presence of H_2S was maintained under reflux for 20 h by the use of a dry ice/ethanol cooled cold-finger condenser. Filtration and combination with the residue obtained upon solvent removal gave 3.60 g (99%) of crude thiadiazolidine, mp 162–167 °C. Recrystallization from benzene/acetone gave the following: mp 170–172 °C;[8,9] ^1H NMR ($CDCl_3$) δ 1.6–3.0 (m, ca. 26 H), 3.50 (br s, 2 H); IR (cm^{-1}, KBr pellet) 3290, 2900, 2830, 1460, 1430, 1400. This compound decomposed in solution.

2',5'-Dihydro-5-bromoadamantanespiro-2'-(1',3',4'-thiadiazine)-5'-spiro-5''/7''-bromoadamantane. A solution of 1.0 g (2.05 mmol) of thiadiazolidine in 100 mL of benzene was mixed dropwise during 40 min with a suspension of 1.2 g (12 mmol) of calcium carbonate in 20 mL of benzene, to which 1.18 g (2.67 mmol) of lead tetraacetate had been added in portions at 0 °C, and the solution stirred for 20 min. After further stirring of this mixture for 44 h, 25 mL of water was added, and the brown precipitate filtered off. The aqueous layer was saturated with NaCl and extracted with ether. The combined organic layers were dried and concentrated to give 0.97 g (98%) crude thiadiazine, decomp point 220–223 °C.[9] Recrystallization from hexane/benzene gave the following: ^1H NMR ($CDCl_3$) δ 1.25–3.05 (m, ca. 22 H), 3.25 (m, 2 H), 3.37 (m, 2 H); IR (cm^{-1}, KBr pellet) 2940, 2850, 1745, 1595, 1470, 1440.

5-Bromoadamantylidene-5'/7'-bromoadamantane (7a/7b). A 0.50-g (1.90-mmol) sample of triphenylphosphine and 0.49 g (1.01 mmol) of thiadiazine were intimately mixed and heated for 16 h at 110–120 °C. Silica gel chromatography (80:20 hexane/ether) gave 0.23 g (53%) dibromolefines **7a** and **7b**. This mixture of isomers melted over the broad range of 185–240 °C.[8,9]

5,5'-7'-Dideuterioadamantylideneadamantane (2a/2b). A 0.173-g (0.224-mmol) sample of tri-*n*-butyltin chloride in 1 mL of dry ether was added under N_2 to 12 mg (0.285 mmol) of lithium aluminium deuteride (Aldrich, 95%) in 3 mL of dry ether. After adding 109 mg (0.256 mmol) of **7a**/**7b**, the mixture was stirred and refluxed for 30 h, then cooled to room temperature, and treated dropwise with 2 mL of D_2O. Pouring into 2 mL of water, extracting with 10 mL of hexane in several portions, drying, and concentrating yielded a residue which was chromatographed on silica gel (hexane eluant) to give 46 mg (67%) of **2a**/**2b**. Sublimation led to a material melting over the range 180–187 °C, which was analyzed by mass spectroscopy for 91% d_2, 9% d_1, and no detected d_0.

4(e)-Chloroadamantylideneadamantane (8).[10] A 850-mg (5.88-mmol) sample phenylsulfenyl chloride[11] was added dropwise to 709 mg (2.64 mmol) of **1** in 10 mL of methylene chloride, and the orange mixture was stirred until TLC indicated complete consumption of **1** (18 h). Concentrating the mixture yielded a residue which was dissolved in 10 mL of carbon tetrachloride and treated with an excess of bromine. Filtration gave the bromonium salt which was repeatedly washed with CCl_4/Br_2 to remove the last traces of diphenyl disulfide. Addition of ether decomposed the salt, and extraction with sodium thiosulfate solution, drying, and concentrating gave 760 mg (95%) of **8**: mp 144.5–147 °C;[8,9] ^1H NMR ($CDCl_3$) δ 1.1–2.6 (complex, ca. 22 H), 2.6–3.2 (m, 3 H), 4.12 (br s, 1 H); IR (cm^{-1}, KBr pellets) 2960, 2920, 2840, 1448, 1085, 795.

4(e)-Deuterioadamantylideneadamantane (3). A 250.3-mg (0.83-mmol) sample of **8** was added to a mixture of 131 mg (3.1 mmol) of $LiAlD_4$ and 107.4 mg (0.33 mmol) of tri-*n*-butyltin chloride in 25 mL of dry ether. After the mixture was refluxed for 86 h, 30 mL of D_2O was added and the mixture poured into 40 mL of water. The product was found to contain starting material, so the process was repeated, giving 106 mg of **3** (48%).[8] Crystallization from methanol and sublimation gave the following: mp 165.5–168 °C; mass spectral analysis, 97% d_1, 3% d_0; ^2H NMR (^1H decoupled) (C_6F_6) δ 1.86 (s) (XL-100 instrument).

Bis(bicyclo[3.3.1]non-9-ylidene) (4) was prepared by the method of Schaap and Faler.[6] The ketazine, mp 152–153 °C (hexane),[8] was carried on to **4** without purification of intermediate in 28% yield, giving material with a melting point of 142–143 °C[8] (lit.[12] mp 144–146 °C).

The preparations of compounds **5**[13] and **6**[14] have been previously described, and **9** was a gift from Professor H. Wynberg.

Results. ESR and ENDOR Spectra

Radical Cations of Monoolefins. The ESR spectrum of $1^{+\cdot}$ observed in the earlier work was an ill-resolved series of broad

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[6] Schaap, A. P.; Faler, G. R. *J. Org. Chem.* **1973**, *38*, 3061.

[7] Geluk, H. W.; Schlatmann, J. L. M. A. *Tetrahedron* **1968**, *24*, 5369.

[8] Empirical formula established by high-resolution mass spectroscopy; AEI MS-902 instrument.

[9] Satisfactory analysis obtained by Spang Microanalytical Laboratories, Eagle Harbor, MI.

[10] Bolster, J.; Kellogg, R. M.; Meijer, E. W.; Wynberg, H. *Tetrahedron Lett.* **1979**, 285.

[11] Harpp, D. N.; Friedlander, B. T.; Smith, R. A. *Synthesis* **1979**, 181.

[12] Keul, H. *Chem. Ber.* **1975**, *108*, 1207.

[13] Nelsen, S. F.; Hollinsed, W. C.; Kessel, C. R.; Calabrese, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 7876.

[14] For nonspectral examples, see: Nelsen, S. F.; Kessel, C. R.; Grezzo, L. A.; Steffek, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 5482.

Table I. Proton, Deuteron, and ^{14}N Coupling Constants (a_X in mT) and g Factors for the Radical Cations of Adamantylideneadamantane (**1**), its Deuterio Derivatives **2a**/**2b** and **3**, Bis(bicyclo[3.3.1]non-9-ylidene) (**4**) and 9.9′-Bis(9-azabicyclo[3.3.1]nonane) (**5**)

X	$1^{+\cdot}$	$2a^{+\cdot}/2b^{+\cdot}$	$3^{+\cdot}$	$4^{+\cdot}$	$5^{+\cdot}$
$H_\beta{}^{eq}$	0.058 (4 H)[a]	0.057 (4 H)	0.056 (4 H)	0.105 (4 H)	0.099 (4 H)
$H_\gamma{}^{eq}$	0.327 (8 H)	0.325 (8 H)	0.329 (7 H) 0.049 (1 D)	0.370 (8 H)	0.128 (8 H)
$H_\gamma{}^{ax}$	0.047 (8 H)	0.046 (8 H)	0.046 (8 H)	0.055 (8 H)	0.059 (8 H)
$H_\delta{}^{eq}$	0.605 (4 H)	0.602 (2 H) 0.095 (2 D)	0.609 (4 H)	0.320 (4 H)	0.160 (4 H)
$H_\delta{}^{ax}$				<0.020 (4 H)[b]	0.027 (4 H)
H_ϵ	0.012 (4 H)	0.012 (4 H)	0.012 (4 H)[b]		
N					1.33 (2 N)
g	2.0032	2.0032	2.0032	2.0033	2.0038

[a] Number of equivalent nuclei in the set is given in parentheses. [b] Unresolved hyperfine splitting.

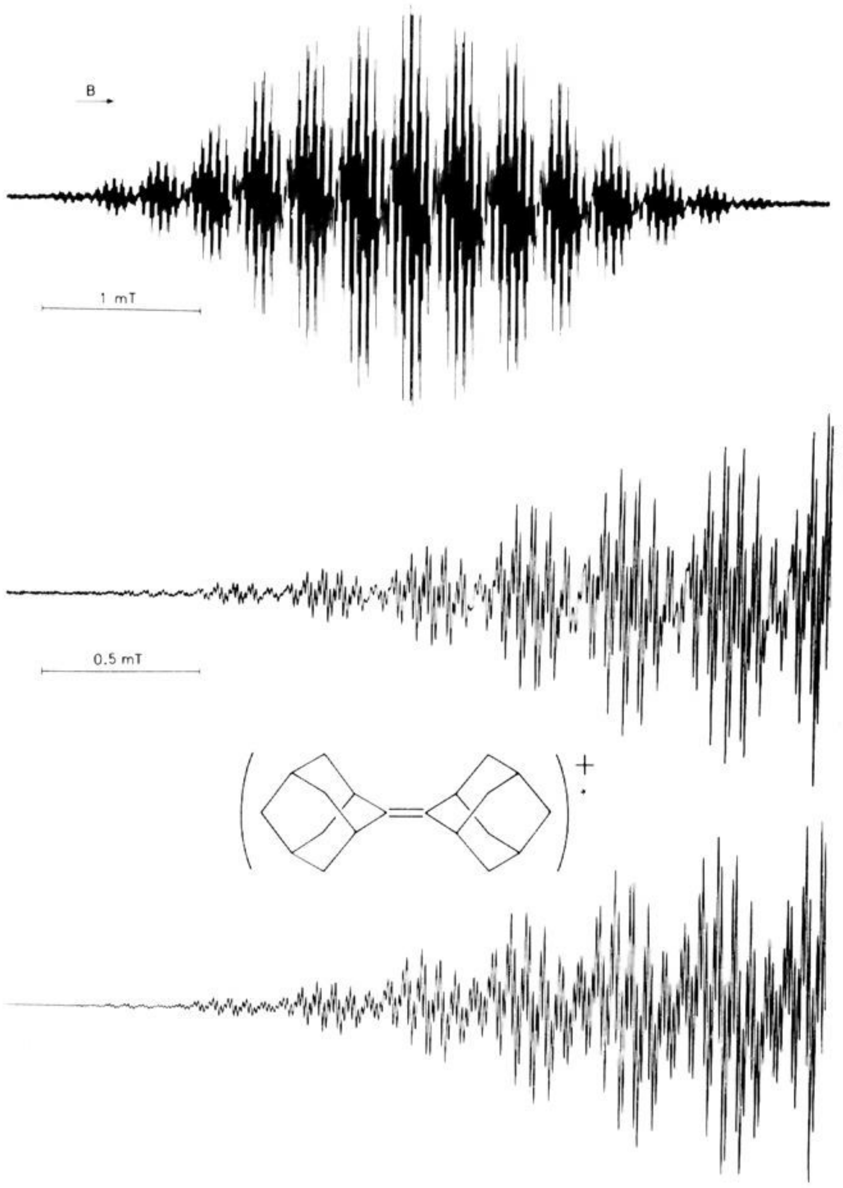

Figure 1. ESR spectra of the radical cation of adamantylideneadamantane (**1**): top, experimental spectrum (solvent = $CH_2Cl_2/CF_3COOH/(CF_3CO)_2O$ (10:1:1); temperature = 193 K); middle, low-field half of the spectrum at an expanded scale; bottom, half of the spectrum simulated with the use of the coupling constants listed in Table I (line shape Lorentzian; line width = 0.009 mT).

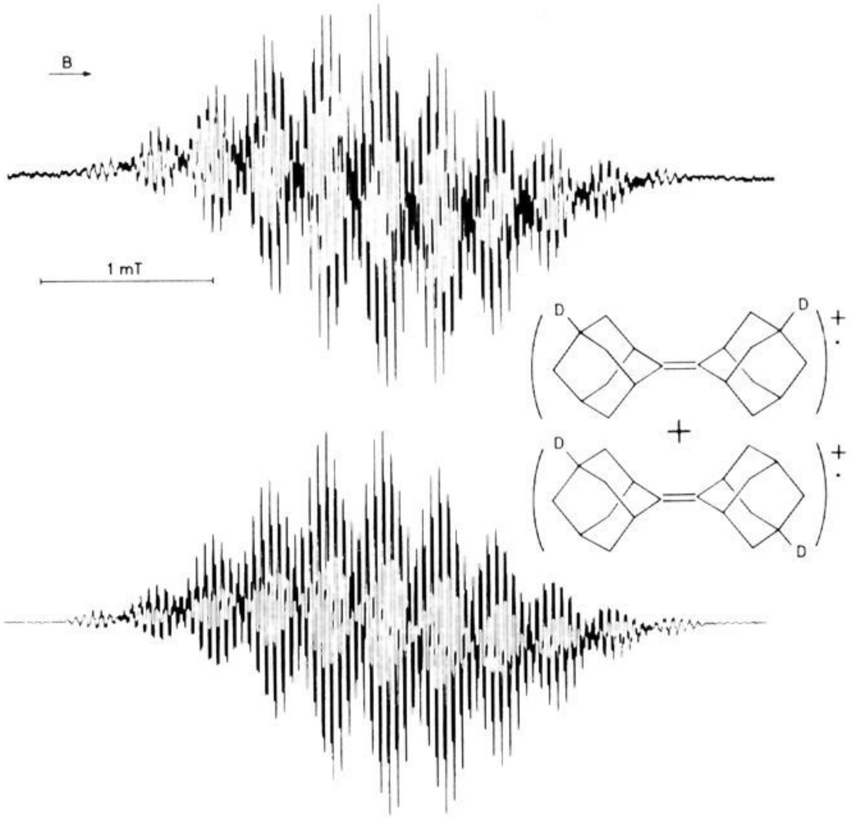

Figure 2. ESR spectra of the radical cations of the dideuterioadamantylideneadamantanes **2a**/**2b** (mixture): top, experimental spectrum (solvent = $CH_2Cl_2/CF_3COOH/(CF_3CO)_2O$ (10:1:1); temperature = 193 K); bottom, spectrum simulated with the use of the coupling constants listed in Table I (line shape Lorentzian; line width = 0.011 mT).

lines separated by 0.3 mT (1 mT = 10 G).[5] This spectrum was apparently being broadened by the exchange between the neutral compound **1** and its radical cation $1^{+\cdot}$. In the present work, $1^{+\cdot}$ was generated by electrolytic oxidation of **1** in a cyclindrical cell containing a gold helical anode and a platinum wire cathode along the axis. A mixture of CH_2Cl_2, CF_3CO_2H, and $(CF_3CO)_2O$ in a volume ratio 10:1:1 served as the solvent.[15] Under these conditions a relatively high and steady concentration of $1^{+\cdot}$ was obtained, provided that the temperature remained below 213 K. The ESR spectrum of $1^{+\cdot}$, shown in Figure 1, consists of hundreds of well-resolved lines. Analysis of this complex hyperfine pattern yields two coupling constants of 0.327 and 0.047 mT, each for a set of eight equivalent γ-protons, and three coupling constants of 0.605, 0.058, and 0.012 mT, each for one of the remaining sets of four equivalent protons. The precision of this analysis is demonstrated by displaying the low-field half of the spectrum vs. the corresponding computer simulated curve (Figure 1).

In order to secure the assignment of the coupling constants, we prepared a mixture of 5,5′- and 5,7′-dideuterioadamantylideneadamantanes (**2a**/**2b**) and the 4(e)-deuterio derivative (**3**). The mixture **2a**/**2b** was produced by a tri-*n*-butyltin deuteride reduction of the mixture **7a**/**7b** of the corresponding dibromo compounds; the latter was obtained from 5-bromo-2-adamantanone by the methodology employed for the synthesis of **1**.[6] Derivative **3** was prepared in modest yield, but with excellent incorporation of deuterium, by tri-*n*-butyltin deuteride reduction of the 4(e)-chloro compound **8**.[10] (For details of the syntheses of **2a**/**2b** and **3**, see Experimental Section.) Although the reaction of **8** with tri-*n*-butyltin deuteride proceeds through the radical centered at carbon atom C(4) and might in principle give a mixture of 4(e) and 4(a) isomers, one expects a predominant approach of the large tin-containing reagent from the less hindered equatorial face of the molecule to yield **3**. Actually, only one type of deuterium was found by proton-decoupled ^2H NMR and by ESR spectroscopy (vide infra).

The ESR spectra of the radical cations $2a^{+\cdot}/2b^{+\cdot}$ and $3^{+\cdot}$, generated electrolytically from the corresponding neutral compounds under the same conditions as $1^{+\cdot}$, are presented in Figures 2 and 3, respectively. As might be expected, the two isomeric species in the mixture $2a^{+\cdot}/2b^{+\cdot}$ gave rise to indistinguishable hyperfine patterns. Deviations of the curves computed for $2a^{+\cdot}$

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(15) Ohya-Nishiguchi, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2064.

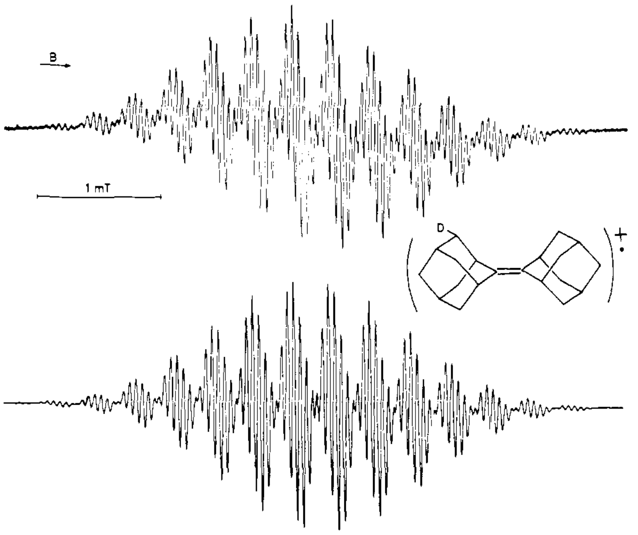

Figure 3. ESR spectra of the radical cation of the deuterioadamantylideneadamantane **3**: top, experimental spectrum (solvent = $CH_2Cl_2/CF_3COOH/(CF_3CO)_2O$ (10:1:1); temperature = 193 K); bottom, spectrum simulated with the use of the coupling constants listed in Table I (line shape Lorentzian; line width = 0.015 mT).

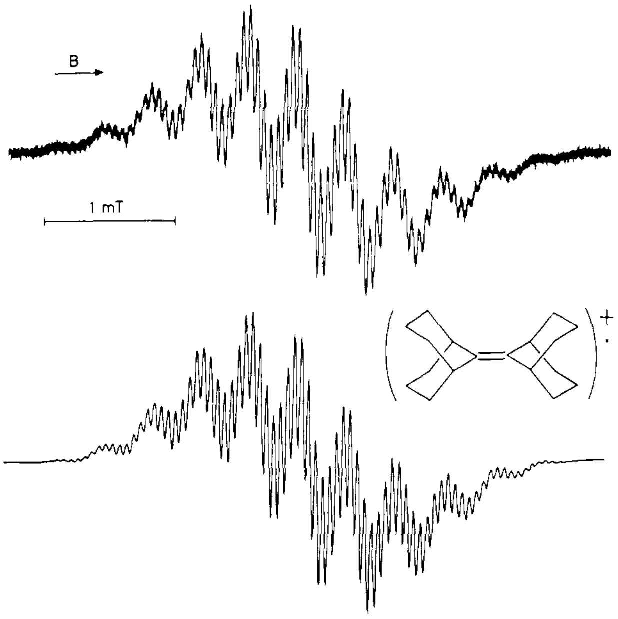

Figure 4. ESR spectrum of the radical cation of 9,9′-bis(bicyclo[3.3.1]non-9-ylidene) (**4**): top, experimental spectrum (solvent = $CH_2Cl_2/CF_3COOH/(CF_3CO)_2O$ (10:1:1); temperature = 203 K); bottom, spectrum simulated with the use of the coupling constants listed in Table I (line shape Lorentzian; line width = 0.030 mT).

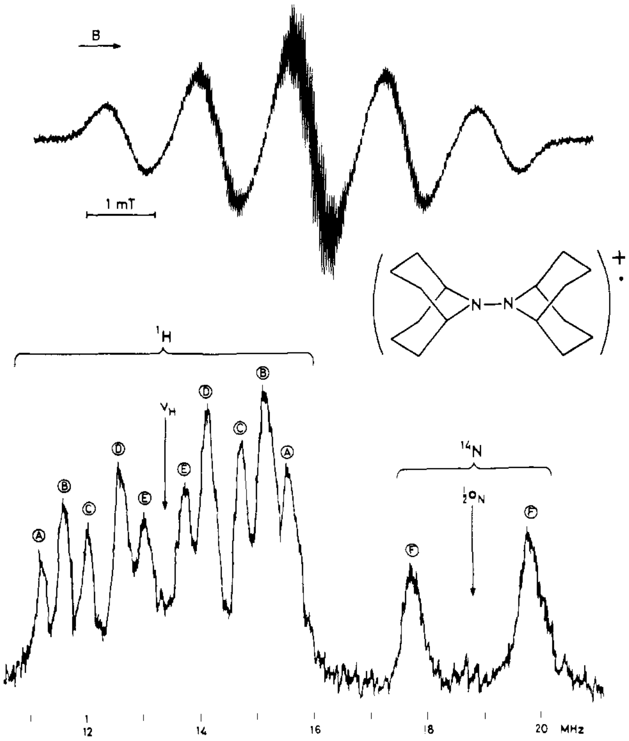

Figure 5. Top: ESR spectrum of the radical cation of 9,9′-bis(9-azabicyclo[3.3.1]nonane) (**5**) (solvent = CH_2Cl_2; temperature = 243 K). Bottom: the corresponding ENDOR spectrum.

or $\mathbf{2b}^{+\cdot}$ (Figure 2) and for $\mathbf{3}^{+\cdot}$ (Figure 3) from the experimental ESR spectra are caused by isotopic impurities, the presence of which was not allowed for in the simulations. These impurities are monodeuteriated (9%) and undeuteriated material (3%) in the case of **2a**/**2b** and **3**, respectively.

Table I collects the hyperfine data and *g* factors for $\mathbf{1}^{+\cdot}$, $\mathbf{2a}^{+\cdot}/\mathbf{2b}^{+\cdot}$, and $\mathbf{3}^{+\cdot}$. On passing from $\mathbf{1}^{+\cdot}$ to $\mathbf{2a}^{+\cdot}/\mathbf{2b}^{+\cdot}$, the set of protons exhibiting the largest coupling constant (0.605 mT) is reduced from four to two, and an additional hyperfine splitting of 0.095 mT, due to the two equivalent δ-deuterons, appears. The change from $\mathbf{1}^{+\cdot}$ to $\mathbf{3}^{+\cdot}$, on the other hand, involves the second largest coupling constant (0.327 mT); the number of pertinent γ-protons decreases from eight to seven, and a splitting of 0.049 mT by one γ-deuteron in the equatorial position is observed. This leads to an unambiguous assignment of the values of 0.605 and 0.327 mT to the four δ-protons and the eight *equatorial* γ-protons, respectively. The latter assignment requires that the second eight-proton coupling constant of 0.047 mT is due to the *axial* γ-protons. An ambiguity still remains with respect to the two four-proton coupling constants of 0.058 and 0.012 mT. INDO calculations on a structurally related radical[16] strongly suggest that the larger of the two values should be assigned to the β-protons, leaving the smaller one for the ϵ-protons.

The ESR spectrum of $\mathbf{4}^{+\cdot}$, obtained by the same experimental procedure as for the other olefin radical cations, is shown in Figure 4. Its moderately resolved hyperfine pattern could be fitted by the computed curve reproduced below the experimental spectrum. The simulation employed two coupling constants of 0.370 and 0.055 mT, each for a set of eight equivalent γ-protons, and two coupling constants of 0.320 and 0.105 mT, each for a set of four equivalent protons. A further hyperfine splitting by the third set of four equivalent protons does not exceed 0.020 mT and is, consequently, masked by the line width (0.030 mT).

The assignment of the coupling constants for $\mathbf{4}^{+\cdot}$ was assisted by comparison with the corresponding values for $\mathbf{1}^{+\cdot}$. It is indicated in Table I which, in addition to the data for $\mathbf{1}^{+\cdot}$ and its deuterated derivatives, includes the coupling constants and *g* factors for $\mathbf{4}^{+\cdot}$, as well as those for the radical cation ($\mathbf{5}^{+\cdot}$) of the hydrazine analogue dealt with in the next section.

Radical Cations of Hydrazines. Solution of $\mathbf{5}^{+\cdot}PF_6^{-}$[3] in CH_2Cl_2 yielded an ESR spectrum consisting of five broad equidistant bands which are characteristic of two equivalent ^{14}N nuclei with a coupling constant of 1.33 mT. Although upon dilution additional splittings by protons were observed, the resolution was insufficient for a reliable analysis. The pertinent proton coupling constants could, however, be determined by use of the ENDOR technique. Figure 5 reproduces both the ESR and ENDOR spectra taken of a highly diluted solution of $\mathbf{5}^{+\cdot}$ in CH_2Cl_2 at 243 K. The five pairs of ENDOR signals in the frequency range of 11–16 MHz, which are denoted A to E, arise from five sets of equivalent protons. They are centered at ν_H = 13.4 MHz, the frequency of the free proton at a magnetic field of 0.315 T (1 T = 10^4 G), and correspond to coupling constants of 0.160, 0.128, 0.099, 0.059,

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[16] Lloyd, R. V.; Rogers, M. T. *Chem. Phys. Lett.* **1972**, *17*, 428.

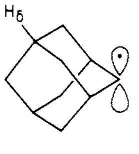
and 0.027 mT, respectively. Although the intensity of an ENDOR signal is not a quantitative measure of the number of protons giving rise to it, one may reasonably attribute the strongest signals B and D to the two sets of eight equivalent γ-protons (0.128 and 0.059 mT), and A, C, and E to three sets of four equivalent protons (0.160, 0.099, and 0.027 mT). Such a choice is consistent with the ESR spectrum, as confirmed by computer simulation of the central band which exhibits the best resolution of the proton hyperfine structure. A more specific assignment of the five coupling constants to individual sets of equivalent protons has again been guided by analogy with the hyperfine data for **1**$^{+}\cdot$ (Table I).

Apart from the five pairs of proton signals, the ENDOR spectrum of **5**$^{+}\cdot$ reveals an additional pair of signals at a higher frequency (Figure 5). The separation of these signals, which are denoted F, is ca. 2.1 MHz; it is slightly larger than twice the frequency of the free ^{14}N nucleus at 0.315 T (ν_N = 0.95 MHz).[17] The two signals are centered at 18.8 MHz, which corresponds to half of the ^{14}N coupling constant, $^1/_2 a_N$ = 0.67 mT. Within the limits of experimental error (±0.01 mT) the a_N value determined by the ENDOR technique (1.34 mT) thus agrees with that provided by the ESR spectroscopy (1.33 mT).

The ESR spectrum obtained from the PF_6^- salt of **6**$^{+}\cdot$ in solution closely resembles that of **5**$^{+}\cdot$. It is also composed of five broad bands which are separated by 1.33 mT, the coupling constants of two equivalent ^{14}N nuclei. However, in contrast to **5**$^{+}\cdot$, neither partial resolution, indicative of the proton hyperfine splittings, nor an ENDOR spectrum could be observed in this case.

Discussion. ESR and ENDOR Spectra

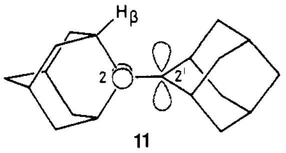
The prominent feature of the hyperfine data for the radical cation (**1**$^{+}\cdot$) of adamantylideneadamantane is the coupling constant of 0.605 mT which is surprisingly large for the remote δ-protons. The most appropriate value to be compared with this coupling constant is 0.355 mT found in the ENDOR spectrum of the 2-adamantyl radical (**10**·)[16] and assigned to the two equivalent



10·

δ-protons on the basis of INDO calculations. Although one may expect the spin population in one moiety of **1**$^{+}\cdot$ to be only half as high as in **10**·, the δ-proton coupling constant for **1**$^{+}\cdot$ is actually much larger than for **10**·, corresponding to a 3.4-fold more effective proportionality factor. It is known that such a factor is considerably increased for radical cations relative to neutral radicals.[18] In the case of **1**$^{+}\cdot$, this increase seems to be accentuated, presumably by much higher than usual positive charge. A further requirement found experimentally for the occurrence of a large δ-proton coupling constant is the collinearity of C(5)–H_δ with the C(3)–C(4) and C(1)–C(9) bonds; such a structure should provide a substantial overlap with the $2p_z$ AO at C(2). Since in the radical cation (**4**$^{+}\cdot$) of bis(bicyclo[3.3.1]non-9-ylidene) the bridging C(6) methylene group enforcing the pertinent alignment is absent, the rings distort to minimize the nonbonded interaction (see the X-ray crystallographic structure of **5**$^{+}\cdot$, the radical cation of the hydrazine analogue[13]). Accordingly, on passing from **1**$^{+}\cdot$ to **4**$^{+}\cdot$ the δ-proton coupling constant decreases from 0.605 to 0.320 mT. A strong angular dependence of this kind has been previously noted for conjugative effects transmitted through σ bonds.[14]

Molecule **1** is strained by the close approach of the β-hydrogens, the separation of which (190 pm)[19] falls significantly short of twice the van der Waals radius of the H atom (240 pm). Moreover, removal of an electron to form **1**$^{+}\cdot$ greatly weakens the π bond. Despite these arguments, a substantial twist about the central C(2)–C(2′) bond, as indicated in **11**, seems improbable. Four pieces of experimental evidence point to an essentially planar one-π-electron system in **1**$^{+}\cdot$.



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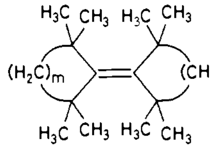
First, it has recently been shown by studies on the radical cations of sterically hindered bicycloalkylidenes **12**, **13**, and **14**[20] that a



12 m = n = 1
13 m = 1, n = 2
14 m = n = 2

large twist about the π bond, concomitant with a decrease in the overlap of the $2p_z$ AO's at the sp^2-hybridized carbon atoms, affects the exchange of the unpaired electron between the two alkylidene moieties of the molecule. Consequently, the exchange becomes slow on the hyperfine time scale (10^6–10^8 s^{-1}) and the spin population appears to be localized on one moiety. Such a localization was not observed in the ESR spectra of **1**$^{+}\cdot$ which exhibit a uniform hyperfine interaction with the protons of both adamantylidene moieties.

Second, the relatively small value of the β-proton coupling constant (0.058 mT) is consistent with the β-hydrogen lying in the nodal plane of the π system. By contrast, distortion of this system from planarity would yield a larger value of this coupling constant.[21]

Third, it has been concluded[13] that the $2p_z$ axes at the two nitrogen atoms are parallel in the radical cation (**5**$^{+}\cdot$) of 9,9′-bis(8-azabicyclo[3.3.1]nonane). Like **1**$^{+}\cdot$, this radical cation has formally half a π bond, but since antibonding orbitals are destabilized slightly more than bonding orbitals are stabilized, one expects the "three-electron π bond" in **5**$^{+}\cdot$ to be even weaker than the "one-electron π bond" in **1**$^{+}\cdot$. (The strength of the π bond in the radical cations of hydrazines has been estimated as 19 kcal/mol (=79.5 kJ/mol).) This comparison suggests that the $2p_z$ orbitals at atoms C(2) and C(2′) in **1**$^{+}\cdot$ ought to be parallel as well.

Fourth, the rapid electron transfer between **1** and **1**$^{+}\cdot$ (cf. the section on cyclic voltammetry) can be regarded as evidence against different geometries of the two species, i.e., the one-π-electron system of **1**$^{+}\cdot$ should be essentially as planar as that of the two-π-electron system of **1**.

As for the coupling constants of the γ-protons in **1**$^{+}\cdot$, it is noteworthy that the value of 0.327 mT for the protons in the equatorial positions is 7 times as large as the corresponding value of 0.047 mT for those in the axial positions. Molecular models of **1** indicate that there is a W like arrangement of a C–H_γ^{eq} bond and a $2p_z$ axis at the olefinic carbon atom bearing a high π-spin population. However, the coplanarity of the W chain required for such an arrangement to be effective in a long-range σ–π delocalization is only approximate. The flattening of the six-membered rings, which accompanies the removal of the bridging C(6) methylene group on going from **1**$^{+}\cdot$ to **4**$^{+}\cdot$, increases slightly both coupling constants of equatorial and axial γ-protons (Table

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(17) The ENDOR experiment was performed on the central ESR band, i.e., for the component $M_I = 0$ of the ^{14}N nucleus. The increase in the separation of the signals F beyond $2\nu_N$ is due to second-order shifts. See: Leniart, D. S.; Vendrine, J. C.; Hyde, J. S. *Chem. Phys. Lett.* **1970**, *6*, 637.

(18) See, e.g., Gerson, F. "Hochauflösende ESR-Spektroskopie, dargestellt anhand aromatischer Radikalionen"; Verlag Chemie: Weinheim, 1967. English translation: "High Resolution ESR-Spectroscopy"; Verlag Chemie: Weinheim (Wiley: New York), 1970.

(19) Lidd, R. D.; Mann, O. E. *J. Chem. Phys.* **1958**, *28*, 572.

(20) Gerson, F.; Lopez, J.; Krebs, A.; Rüger, W. *Angew. Chem.* **1981**, *93*, 106; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 95.

(21) The coupling constants of the β-protons are proportional to $\cos^2 \theta$, where θ is the dihedral angle between the C–H_β bond and the $2p_z$ axis at the adjacent carbon π center.[22]

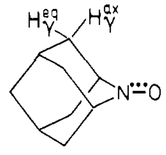
(22) Heller, C.; McConnell, H. M. *J. Chem. Phys.* **1960**, *32*, 1535. Horsfield, A.; Morton, J. R.; Whiffen, D. H. *Mol. Phys.* **1961**, *4*, 425.

Table II. CV Data for Olefins

compd	$E^{\circ\prime}$,[a] V	$\Delta(\Delta G^{\circ})$,[b] kcal/mol (1 kcal = 4.184 kJ)
1	1.45	[0]
4	1.49	+0.9
7a/7b	*c*	*c*
8	1.61[d]	+3.7
9	1.35	−2.3

[a] At a Pt electrode; solvent acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate; vs. SCE; scan rate 20–200 mV/s unless otherwise indicated. [b] $[E^{\circ\prime} - E^{\circ\prime}(1,1^{+})]$ 23.06; a positive entry means it is thermodynamically more difficult to remove an electron than from 1. [c] No reduction peak observed, even at 10-V/s scan rate. $E_p^{ox} = 1.73$ V at 200-mV/s scan rate, corresponding to $\Delta(\Delta G^{\circ}) > 9$ kcal/mol (see text). [d] At 10-V/s scan rate, where $E_p^{ox} - E_p^{red} = 75$ mV. No reduction wave observed at 0.5-V/s scan rate or below.

I), but their ratio remains nearly unchanged. To our knowledge, experimental data to be compared with these results are scarce. The closest structural analogy is provided by the 2-azaadamantyl-2-oxyl radical (**15·**)[23] despite the fact that this radical is



15·

presumably bent at the nitrogen atom,[24] causing the β-proton splitting to be much larger than in $\mathbf{1}^{+\cdot}$. The equatorial and axial γ-protons in **15·** exhibit the coupling constants of +0.152 and −0.080 mT, respectively; i.e., the ratio of their absolute values is under 2.

The radical cations $\mathbf{4}^{+\cdot}$ and $\mathbf{5}^{+\cdot}$ are isostructural and have essentially the same π charge and geometry. However, it is not surprising that the hyperfine coupling constants for $\mathbf{5}^{+\cdot}$ are on average only half as large as the corresponding values for $\mathbf{4}^{+\cdot}$ (Table I). This finding can be rationalized in terms of the above-mentioned difference in the character of the singly occupied π orbital in $\mathbf{4}^{+\cdot}$ and $\mathbf{5}^{+\cdot}$. The pertinent MO is antibonding for $\mathbf{5}^{+\cdot}$ and, despite the presence of two electronegative nitrogen atoms, lies energetically higher than the corresponding MO for $\mathbf{4}^{+\cdot}$, which has bonding character. (The ionization potential of **5** in the gas phase is 6.94 eV, while the analogous value of **4**, which has not yet been measured, must be close to 7.84 eV obtained for **1**.[25]) Therefore, the energy gap between the highest occupied σ orbital and the "hole" in the π system is smaller for the olefinic radical cation $\mathbf{4}^{+\cdot}$ than for its hydrazine counterpart $\mathbf{5}^{+\cdot}$. This difference leads to a more effective hyperconjugative interaction in $\mathbf{4}^{+\cdot}$ than in $\mathbf{5}^{+\cdot}$ and therewith to the observed larger delocalization onto the alkyl hydrogen atoms.

The *g* factors of $\mathbf{1}^{+\cdot}$ and $\mathbf{4}^{+\cdot}$ (Table I) are rather high, since they exceed that of the free electron ($g_e = 2.0023$) by $\Delta g = 9 \times 10^{-4}$, whereas the Δg values reported for the radical cations of other hydrocarbons are generally in the range of $(2–5) \times 10^{-4}$.[26] This finding is the more unexpected, as the *g* factors should be lower the less extended the π system.[27] Presumably, the high *g* factors of $\mathbf{1}^{+\cdot}$ and $\mathbf{4}^{+\cdot}$ are a consequence of the small energy gap between the half-filled π MO and the highest occupied σ orbital, in accord with the prediction of McConnell and Robertson[28] that a low σ–π transition energy should raise the *g* factor of a radical.

Results and Discussion. Cyclic Voltammetry

The long lifetime of the radical cation ($\mathbf{1}^{+\cdot}$) of adamantylideneadamantane and its analogues in solution allows one to measure the standard potential for an electron loss, $E^{\circ\prime}$, by cyclic voltammetry (CV); the results are summarized in Table II. Because $E^{\circ\prime}$ values for two electron-transfer equilibria are equal to $\Delta(\Delta G^{\circ})$ for the electron transfers, these numbers are thermodynamically meaningful. As expected from their structural similarity, the two monoolefins, adamantylideneadamantane (**1**) and bis(bicyclo[3.3.1]non-9-ylidene) (**4**), exhibit very similar $E^{\circ\prime}$ values. A rapid electron transfer between the neutral molecules and their radical cations (which is consistent with a rather small change in geometry on passing from the former to the latter) is indicated by the observation that the oxidation is reversible even at a scan rate as fast as 100 V/s. On the other hand, the findings that the reversibility remains complete, and no decomposition of the radical cations is observed, when the scan is slowed down to 20 mV/s, points to a high kinetic stability (persistence) of $\mathbf{1}^{+\cdot}$ and $\mathbf{4}^{+\cdot}$.

The introduction of one chlorine atom into the γ-equatorial position of **1** to yield 4(e)-chloroadamantylideneadamantane (**8**) raises ΔG° by 3.7 kcal/mol (=15.5 kJ/mol), thus demonstrating the great sensitivity of this equilibrium to an electron-withdrawing substituent which is rather remote from the π system. The radical cation $\mathbf{8}^{+\cdot}$ is by far less persistent than $\mathbf{1}^{+\cdot}$, and no reduction wave was discerned for it at a scan rate of 500 mV/s. Such a wave could, however, be observed at 10 V/s, allowing the $E^{\circ\prime}$ value to be determined. By contrast, the radical cations produced from the mixture of the 5,5′- and 5,7′-dibromoadamantylideneadamantanes (**7a**/**7b**) did not exhibit a reduction wave even at very fast scan rates. The low persistence of $\mathbf{7a}^{+\cdot}$ and $\mathbf{7b}^{+\cdot}$ thus preclude the determination of $E^{\circ\prime}$. Nevertheless, with the assumption that electron transfer is rapid relative to the scan rate, a value $\Delta(\Delta G^{\circ})$ of 9 kcal/mol (=38 kJ/mol) can be estimated for the introduction of two δ-bromine atoms on going from $\mathbf{1}^{+\cdot}$ to $\mathbf{7a}^{+\cdot}/\mathbf{7b}^{+\cdot}$. These results emphasize the importance of charge delocalization into the σ framework of $\mathbf{1}^{+\cdot}$ and therewith complement the findings by ESR spectroscopy. Examples of a similar effect were recently discussed,[14] in particular the change in $E^{\circ\prime}$ values upon the introduction of two keto groups into the δ positions of **5** to yield **6**. Moreover, the great influence of halogen atom substitution on $E^{\circ\prime}$ values of monoolefin radical cations is reminiscent of the large rate-slowing effect on solvolysis, reported by Schleyer and co-workers for carbenium ions derived from diadamantanes.[29] This effect was observed when bromine replaced hydrogen at positions which are remote from the incipient cationic center but can conjugate through σ bonds with such a center.

Attaching the adamantylidene fragments to the double bond in a way to give bis(homoadamantene) (**9**)[30] renders ΔG° for electron removal 2.3 kcal/mol (=9.6 kJ/mol) more favorable than for **1**. How much of this difference represents destabilization of the neutral olefin (molecule **9** is extremely congested; the compound does not even react with bromine[30b] and how much represents preferential stabilization of the radical cation are not known.

Comparison of the $E^{\circ\prime}$ values for the olefin **4** and its hydrazine analogue **5**[3c] shows that **4** is, by 35.6 kcal/mol (=149 kJ/mol), thermodynamically more difficult to oxidize. A large part of this difference is the higher energy of the uppermost occupied (antibonding) orbital of **5** relative to the corresponding (bonding) orbital of **4**. As pointed out in the previous section, this part can be estimated as 0.9 eV or 20.8 kcal/mol (=86.8 kJ/mol) from the vertical ionization potentials in the gas phase. Another major contribution to the ease of oxidation of **5** in solution is undoubtedly due to the relaxation energy of the radical cation $\mathbf{5}^{+\cdot}$, since, in contrast to the passage from **4** to $\mathbf{4}^{+\cdot}$ (see above), the hydrazine

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(23) Dupeyre, R. M.; Rassat, A. *Tetrahedron* **1978**, *34*, 1501.

(24) For a dicussion, see: Lajzerowicz-Bonneteau, J. "Spin Labeling"; Berliner, L. J., Ed.; Academic Press: New York, 1976; pp 239–249.

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5 undergoes a great change in geometry upon removal of one electron.[31]

It is also of interest to compare the $E^{\circ\prime}$ value of **1** with those of polycondensed aromatic hydrocarbons.[5] Such a comparison reveals that the radical cation $\mathbf{1}^{+\cdot}$ is considerably stabilized by solvation in acetonitrile, since the pertinent value is about 0.36 V or 8.3 kcal/mol (=34.7 kJ/mol) lower for **1** than for an aromatic hydrocarbon of the same ionization potential in the gas phase. The stabilization of the monoolefinic radical cation centers in $\mathbf{1}^{+\cdot}$ by the solvent can be rationalized by the presence of the alkyl groups bearing high positive charges, as indicated by the large coupling constants found in the ESR spectrum for the γ- and δ-protons. In energy terms, the ionization potential of **1** in the gas phase is comparable to that of the 14-π-electron system, phenanthrene, while (owing to the extra stabilization by the solvent) the value $E^{\circ\prime}$ for **1** in solution is equal to that of the 18-π-electron system, 1,2-benzanthracene.[5] Another illustrative example for the surprising ease of electron loss from such monoolefins, which are protected by Bredt's rule, is the value $E^{\circ\prime}$ for the bis(homoadamantane) (**9**); it is the same as that of tetraphenylethylene. In this context, it is noteworthy that the radical cation of the latter compound exhibits no reduction wave in the cyclic voltammogram at a scan rate of 200 mV/s. This behavior contrasts with that of $\mathbf{9}^{+\cdot}$ which, like $\mathbf{1}^{+\cdot}$ and $\mathbf{4}^{+\cdot}$, is stable for tens of seconds under analogous conditions. The much higher persistence of these species is due to the steric protection of the radical and cationic centers by the bulky saturated groups. Such substituents preclude the addition reactions which, in the case of tetraphenylethylene, lead to a rapid decay of the radical cation.

Conclusions

As indicated by the large long-range interaction with the γ- and δ-protons, the unusually great electron demand imposed by the high charge density in the monoolefin radical cation causes a substantial hyperconjugative delocalization of spin and charge into the saturated alkyl substituents. The considerable stabilization of the radical cation by this delocalization is greatly reduced when the γ- or δ-hydrogens are replaced by halogen atoms.

Acknowledgment. This work was supported by the National Science Foundations of the U.S.A. (major instrument program) and Switzerland (Project 2.625.080). R.A. thanks the Romnes Foundation for a scholarship. We are indebted to Professor H. Wynberg for a gift of a sample of **9**.

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Kinetics of Gas Phase Tetramethyldioxetane Decomposition and Chemiluminescence

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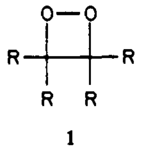
Abstract: Pulsed-laser excitation of overtone vibrations or a weak electronic transition in gas-phase tetramethyldioxetane in combination with temporally and spectrally resolved detection of decomposition product luminescence reveals the presence, along with electronically excited acetone, of an additional emitting species which is not observed in solution studies. The emission is at shorter wavelengths than the acetone phosphorescence, and the emitting species has a zero-pressure decay rate of 0.019 ± 0.014 μs^{-1}. The rapid collisional quenching which occurs on roughly every other encounter ($k_q = 5.6\ \mu s^{-1}\ torr^{-1}$) explains the inability of solution measurements to detect this feature of the tetramethyldioxetane decomposition kinetics. This newly observed component is likely to extend the interpretation of gas-phase decomposition experiments using infrared multiphoton absorption or collisions with fast Xe atoms to excite tetramethyldioxetane.

Dioxetanes (**1**) are four-membered cyclic peroxides which have the intriguing property of efficiently producing electronically excited products upon decomposition and, thus, converting chemical energy to light.[1-4] They are also intermediates in the reaction of singlet oxygen with olefins[2] and are suggested models of bioluminescent processes.[4] The surprising result that dioxetanes produce many more triplet ketone products than excited singlet products continues to stimulate experimental and theoretical efforts to unravel the mechanism of the decomposition. The concerted mechanisms which was first proposed[5] has now given way to one involving a biradical intermediate produced by opening of the O–O bond in the ring,[6,7] but questions of the stability of the biradical remain.[8,9] A GVB–CI calculation by Harding and Goddard[10] predicts a significant local potential energy minimum for the biradical and, in fact, finds the maximum energy along the reaction



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