

and may simply reflect the ratio of the *C* and *B* vibronic terms.

4. Trp also shows L_a -resonant vibronic activity for ν_{8a} - and ν_{8b} -like modes. The strong 220-nm absorption band, identified with the B_b transition, enhances ν_{8a} but not ν_{8b} , consistent with the near-long axis polarization calculated for the transition and the antisymmetric character of ν_{8b} . Strongest enhancement is seen for indole ring modes having substantial pyrrole ring character. These modes are enhanced only weakly in the short-wavelength (~ 195 nm) band, attributed to B_a , which selects for the ν_{8a} and ν_{8b} modes. B_a is suggested to be localized largely on the benzene

ring, while B_b is a more delocalized transition.

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Registry No. H-Phe-OH, 63-91-2; H-Tyr-OH, 60-18-4; H-Trp-OH, 73-22-3; PhOH, 108-95-2; PhOH·Na, 139-02-6; H-Tyr-OH·2Na, 69847-45-6.

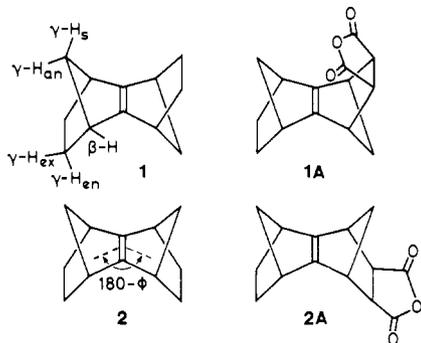
Spin Distributions and Geometries of the Radical Cations of Sesquinorbornenes and Other Polycyclic Tetraalkylethenes

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Contribution from the Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland, the S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, and the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. Received November 25, 1988

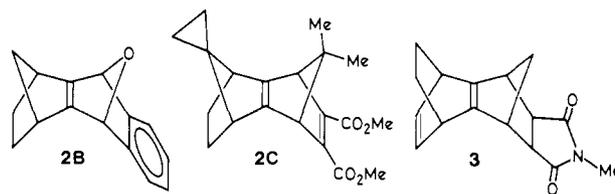
Abstract: The radical cations of *anti*- and *syn*-sesquinorbornenes (**1** and **2**, respectively) and *syn*-sesquinorbornatriene (**4**) have been characterized by their hyperfine data. The proton coupling constants, in millitesla, are as follows: **1**^{•+}, 1.346 (2 γ -*anti*-H), 0.326 (4 β -H), 0.311 (4 γ -*exo*-H), 0.103 (2 γ -*syn*-H), and 0.068 (4 γ -*endo*-H); **2**^{•+}, 0.746 (2 γ -*anti*-H), 0.392 (4 β -H), 0.353 (4 γ -*exo*-H), 0.083 (2 γ -*syn*-H), and 0.076 (4 γ -*endo*-H); **4**^{•+}, 1.066 (2 γ -*anti*-H), 0.252 (4 β -H), 0.090 (2 γ -*syn*-H), and 0.064 (4 vinylic H). Hyperfine data are also reported for the radical cations of isopropylideneadamantane (**6**), sesquihomoadamantane (**7**), and dimethylhomoadamantane (**8**). Spin delocalization into the polycyclic alkyl groups is discussed, as well as the geometry of **1**^{•+}, **2**^{•+}, and **4**^{•+}. Comparison of the vertical ionization potentials in gas phase with oxidation potentials $E^{\circ'}$ in solution indicates that **1** and **2** have comparable relaxation energies.

Several derivatives of *anti*-sesquinorbornene (**1**) have a nearly planar geometry at the two olefinic carbons, as do ethenes with less constrained C=C—C bond angles. According to X-ray crystallography, the internorbornene dihedral angle $180 - \phi$ is 177.9° or more (i.e., out-of-plane deformation $\phi = 2.1^\circ$ or less) for **1A**¹ and five similar adducts having *syn*-alkyl groups at C(7)



of the substituted norbornene moiety.² However, bending must be rather easy at the olefinic carbon atoms of **1**, since ϕ values of 13.2° have been determined by X-ray crystallography for its *exo*-4-nitrophenylmaleimide and *N*-methyltriazolinedione adducts.³ Derivatives of *syn*-sesquinorbornene (**2**) are generally more bent; **2A**¹ and five similar adducts^{1,2,4} all exhibit angles ϕ of 15.5 – 18° . Even larger values of ϕ have been found for derivatives of **2** having

additional unsaturated bonds, 22.1° for **2B**⁵ and 21.8° for **2C**.⁶



It has also been shown that the C=C—C angle restriction at the junction of the two norbornene moieties in **2** is not necessary for producing substantial ϕ values in derivatives of fused norbornenes. Thus **3** has $\phi = 11.8^\circ$,⁷ four compounds with bicyclo[3.2.1] frameworks fused *syn* at the norbornene moiety exhibit ϕ values in the range 9.3 – 11.8° ,⁸ and several compounds with monocyclic

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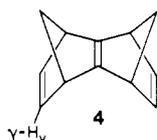
[†] Universität Basel.

[‡] University of Wisconsin.

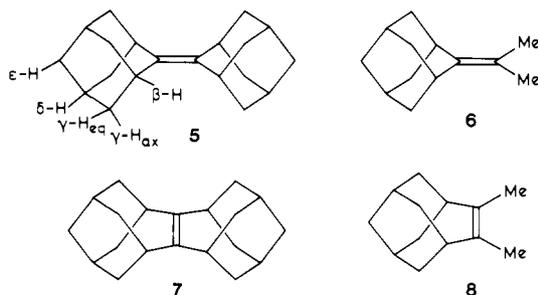
[§] The Ohio State University.

six-membered rings fused to such a moiety present angles ϕ ranging from 4.5 to 10°. The reasons for the endo-pyramidalization at the olefinic carbons have received extensive discussion which has been summarized and continued by Houk and co-workers.¹⁰ Not surprisingly, **2** and its derivatives add reagents to their unusually reactive double bond from the exo face.^{1,10,11} On the other hand, Bartlett and co-workers showed that the hydrogen atom abstracted from the solvent by the triplet state of **2** is incorporated at the endo face,¹² thus indicating a reversal of the pyramidalization upon the excitation of an electron from the π - to the π^* -orbital. Such a reversal is regarded as being theoretically reasonable.¹⁰

Here, we report on the ESR spectra of the radical cations of **1**, **2**, and the *syn*-sesquinorbornatriene (**4**),¹³ which is expected



to be more strongly bent at the central double bond than its monoene counterpart **2**. We discuss the hyperfine data for **1**^{•+}, **2**^{•+}, and **4**^{•+} in the light of their geometry at the carbon atoms of this bond. Also dealt with in the present paper are the radical cations of other ethenes substituted by polycyclic alkyl groups, such as those of adamantylideneadamantane (**5**),^{14,15} isopropylideneadamantane (**6**),¹⁶ sesquihomoadamantane (**7**),¹⁷ and 1,2-dimethylhomoadamantane (**8**).¹⁸



As in the case of **5**^{•+}, the low-lying "orbital hole" in the ethene π -system of **1**^{•+}, **2**^{•+}, **4**^{•+} (central double bond), and **6**^{•+}–**8**^{•+} should partially be filled by a transfer of electrons from the σ -orbitals

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Table I. Proton Coupling Constants (millitesla) and *g* Factors for the Radical Cations of *anti*- and *syn*-Sesquinorbornenes (**1** and **2**, respectively), *syn*-Sesquinorbornatriene (**4**), and Sesquibicyclo[2.2.2]octene (**12**)^a

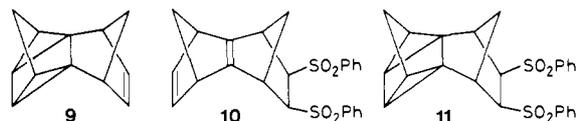
| proton | 1 ^{•+} | 2 ^{•+} | 4 ^{•+} | 12 ^{•+} ^b |
|--------------|------------------------|------------------------|------------------------|--------------------------------------|
| β | 0.326 (4 H) | 0.392 (4 H) | 0.252 (4 H) | <i>c</i> (4 H) |
| γ -an | 1.346 (2 H) | 0.746 (2 H) | 1.066 (2 H) | |
| γ -s | 0.103 (2 H) | 0.083 (2 H) | 0.090 (2 H) | |
| γ -ex | 0.311 (4 H) | 0.353 (4 H) | | 0.390 (8 H) |
| γ -en | 0.068 (4 H) | 0.076 (4 H) | | 0.037 (8 H) |
| γ -v | | | 0.064 (4 H) | |
| <i>g</i> | 2.0029 | 2.0025 | 2.0025 | 2.0024 |

^a Experimental error $\pm 1\%$ in the coupling constants, ± 0.0001 in *g*.
^b Reference 27. ^c Not observed.

of the alkyl groups into the singly occupied orbital (SOMO) π^+ . The σ, π^+ -delocalization bestows thermodynamic stability on these radical cations; for instance, **5** proved to be as easily oxidized as the 18- π -electron aromatic compound 2,3-benzanthracene.¹⁴ Spectroscopic evidence for σ, π^+ -interaction in **5**^{•+} includes the unusually large long-range couplings in the ESR spectrum¹⁵ and the visible region absorption¹⁹ caused by "hyperconjugation transitions" involving a σ, π^+ -charge transfer.²⁰ The radical cations **1**^{•+}, **2**^{•+}, **5**^{•+}, and **7**^{•+} are also kinetically relatively stable (persistent), since their allylic positions are "Bredt-rule protected" from deprotonation. As will be shown, even **4**^{•+}, which contains additional unprotected double bonds, and **6**^{•+} and **8**^{•+}, which bear methyl substituents directly linked to the ethene π -system, are sufficiently long-lived to be studied by ESR spectroscopy.²¹

Results and Discussion

ESR Spectra and Assignments of the Coupling Constants. All radical cations were generated electrolytically in a cylindrical cell containing a helical gold anode and a platinum-wire cathode along the axis.²⁵ Their persistence decreased in the order **7**^{•+} > **5**^{•+} > **2**^{•+} > **1**^{•+} > **8**^{•+} > **6**^{•+} > **4**^{•+}. The radical cation **7**^{•+} was produced under the same conditions as **5**^{•+}, i.e., by oxidation of the neutral compound in a 10:1:1 mixture of CH_2Cl_2 , CF_3COOH , and $(\text{CF}_3\text{CO})_2\text{O}$ at 193 K. These conditions proved not to be optimal for the preparation of the remaining, less-persistent radical cations **1**^{•+}, **2**^{•+}, **4**^{•+}, **6**^{•+}, and **8**^{•+}, which were generated in a 0.1 M solution of Bu_4NClO_4 in CH_2Cl_2 at 173 K. In the case of **4**^{•+}, the isomeric quadricyclane derivative **9** was used in the electrolysis



as the precursor of the radical cation instead of the unstable triene **4** (which could not be transferred from Columbus to Basel). The valence isomerization was catalyzed by Ag^+ ions introduced into the electrolytic cell by adding AgClO_4 to the solution of **9** in

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(21) Although radical cations of unprotected tetraalkylalkenes are strong acids,²² they are persistent in nonbasic solvents at low temperatures, even when the substituents are methyl groups. ESR spectra of such radical cations can be obtained,²³ and chemically reversible oxidation waves are observed with the solvent CH_2Cl_2 containing trifluoroacetic acid (TFA) and its anhydride (TFAA).²⁴

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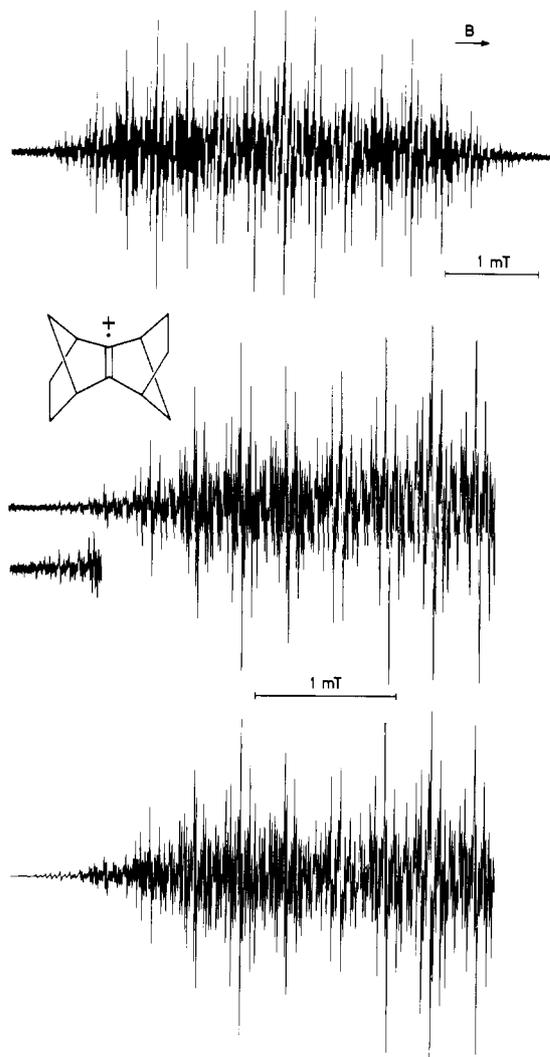
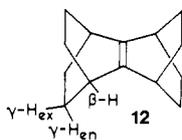


Figure 1. Top: ESR spectrum of $1^{+\bullet}$; solvent, CH_2Cl_2 ; counterion, ClO_4^- ; temperature, 173 K. Middle: left part and center of the spectrum on an expanded magnetic field scale. Bottom: simulation using coupling constants listed in Table I; line shape, Lorentzian; line width, 0.012 mT.

CH_2Cl_2 prior to oxidation. The synthesis of **9** started from di-*exo*-phenylsulfonyl-*syn*-sesquinorbornadiene (**10**), which was photoisomerized to **11** and subsequently treated with sodium amalgam to yield **9**.^{13b}

The ESR spectra of $1^{+\bullet}$, $2^{+\bullet}$, $4^{+\bullet}$, and $7^{+\bullet}$ are shown in Figures 1–4, respectively, along with the simulated derivative curves. The spectrum of $5^{+\bullet}$ has been presented previously;¹⁵ those of $6^{+\bullet}$ and $8^{+\bullet}$ are not reproduced here but can be provided on request.²⁶

Table I lists the hyperfine data for $1^{+\bullet}$, $2^{+\bullet}$, and $4^{+\bullet}$, as well as for the radical cation of sesquibicyclo[2.2.2]octene (**12**), which



has been described elsewhere.²⁷ The prominent features of $1^{+\bullet}$, $2^{+\bullet}$, and $4^{+\bullet}$ are the large values of one coupling constant (1.346, 0.746, and 1.066 mT, respectively) due to two equivalent protons. According to ample experience from the studies of structurally related radical ions²⁸ and as confirmed by theoretical calculations

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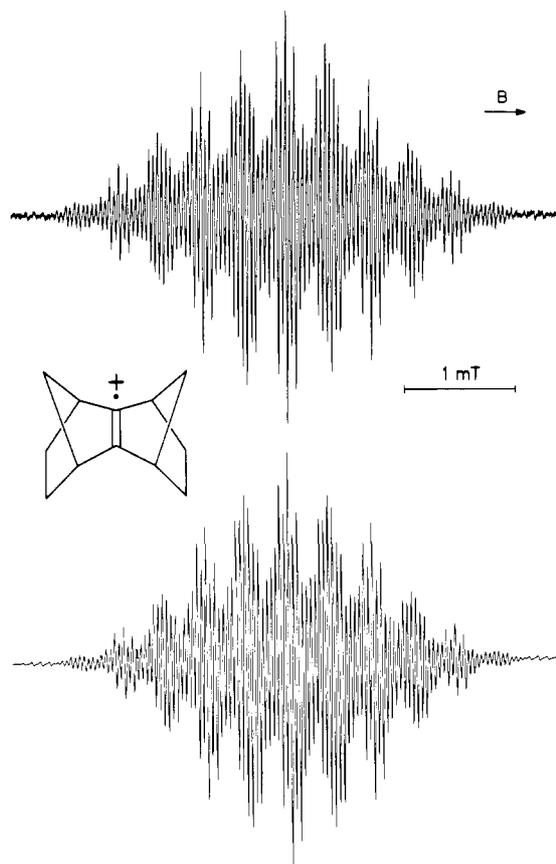


Figure 2. Top: ESR spectrum of $2^{+\bullet}$; solvent, CH_2Cl_2 ; counterion, ClO_4^- ; temperature, 173 K. Bottom: simulation using coupling constants listed in Table I; line shape, Lorentzian; line width, 0.020 mT.

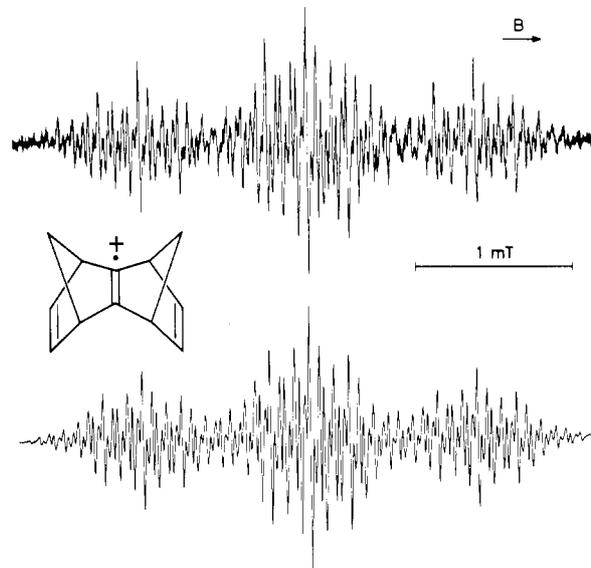
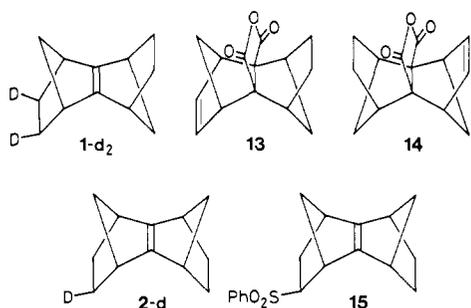


Figure 3. Top: ESR spectrum of $4^{+\bullet}$; solvent, CH_2Cl_2 ; counterion, ClO_4^- ; temperature, 173 K. Bottom: simulation using coupling constants listed in Table I; line shape, Lorentzian; line width, 0.024 mT.

(see below), this large coupling constant must belong to the pair of anti-positioned γ -protons ($\gamma\text{-H}_{\text{an}}$) in the two methano bridging groups. This assignment leaves the second, much smaller two-proton value (0.103, 0.083, and 0.090 mT, respectively) for the pair of γ -protons in the corresponding *syn* positions ($\gamma\text{-H}_{\text{s}}$).

Substantial coupling constants are also expected for the four *exo*-positioned γ -protons ($\gamma\text{-H}_{\text{ex}}$)²⁸ in the two ethano bridging groups of $1^{+\bullet}$ and $2^{+\bullet}$. Since both radical cations have two four-proton values of appropriate magnitude (0.3–0.4 mT), assignments to $\gamma\text{-H}_{\text{ex}}$ had to be based on ESR studies of specifically

deuterated derivatives such as $1-d_2^{2+}$ and $2-d^{2+}$.



The compound $1-d_2$ was prepared from a 3.8:1 mixture of unsaturated anti- and syn-Diels-Alder adducts **13** and **14**, which were obtained by the method of Kopecky and Miller²⁹ from norbornene-2,3-dicarboxylic anhydride.^{11a} As described in the Experimental Section, the synthesis of $1-d_2$ involved a Pt-catalyzed addition of D_2 to the C=C bond in **13** and **14**, followed by a selective hydrolysis of the exo-deuterated anti isomer to its dicarboxylic acid and an oxidative decarboxylation of the acid in two steps. Expectedly, the addition of deuterium atoms occurred from the exo face of the C=C bond in **13**, because the 1H NMR spectra show that the number of protons giving rise to the downfield multiplet³⁰ at δ 1.69 has decreased from four to two on passing from **1** to $1-d_2$. The compound $2-d$ was synthesized from the *exo*-phenylsulfonfyl-*syn*-sesquiorbornene (**15**)^{11c} by reduction with sodium amalgam in MeOD/ Na_2DPO_4 (see Experimental Section). In the 1H NMR spectrum of $2-d$, the relative intensity of the downfield multiplet at δ 1.53 indicates that the one of the four exo protons ($\gamma-H_{ex}$) in **2** was replaced by a deuterium.

Comparison of the ESR spectra of 1^{2+} and $1-d_2^{2+}$ shows that two of the four protons having the coupling constant of 0.311 mT were substituted by two deuterons exhibiting a hyperfine splitting of 0.048 mT. Likewise, by comparison of the ESR spectra of 2^{2+} and $2-d^{2+}$, it is evident that one of the four protons with the coupling constants of 0.353 mT was replaced by a deuterium with a hyperfine splitting of 0.054 mT.²⁶ The assignments to $\gamma-H_{ex}$ resulting therefrom for 1^{2+} and 2^{2+} leave the two remaining four-proton coupling constants for the β -protons ($\beta-H$) at the bridgehead carbon atoms and for the endo-positioned γ -protons ($\gamma-H_{en}$) in the ethano bridging group.

A β -proton coupling constant, $a(\beta-H)$, can be predicted by the use of the well-known relationship³¹

$$a(\beta-H) = B\rho_s\pi \cos^2 \theta \quad (1)$$

where B , $\rho_s\pi$, and θ are the proportionality factor, the π -spin population at the alkyl-substituted carbon center, and the dihedral angle of the C(alkyl)-H(β) bond with the $2p_z$ axis at this center, respectively. Setting $B = 2Q[Me] = 8.7$ mT, $\rho_s\pi = 0.3-0.4$ (see below), and $\theta = 70^\circ$ (as estimated from molecular models), a value of 0.3-0.4 mT is predicted from the coupling constant $a(\beta-H)$ in 1^{2+} and 2^{2+} . This result justifies the assignment made for $\beta-H$ in Table I (1^{2+} , 0.326 mT; 2^{2+} , 0.392 mT). The smallest four-proton coupling constants must thus belong to $\gamma-H_{en}$ (1^{2+} , 0.068 mT; 2^{2+} , 0.076 mT). Their magnitude is in line with the values found for γ -protons in the endo positions of structurally related radical ions.²⁸

Since the dihedral angle θ in 4^{2+} is comparable to that in 1^{2+} and 2^{2+} , the larger of the two four-proton coupling constants (0.252 mT) is also assigned to $\beta-H$, leaving the smaller one (0.064 mT) for the vinylic γ -protons ($\gamma-H_v$) in the two etheno bridging groups. The decrease in the coupling constant on going from $\gamma-H_{ex}$ in 1^{2+}

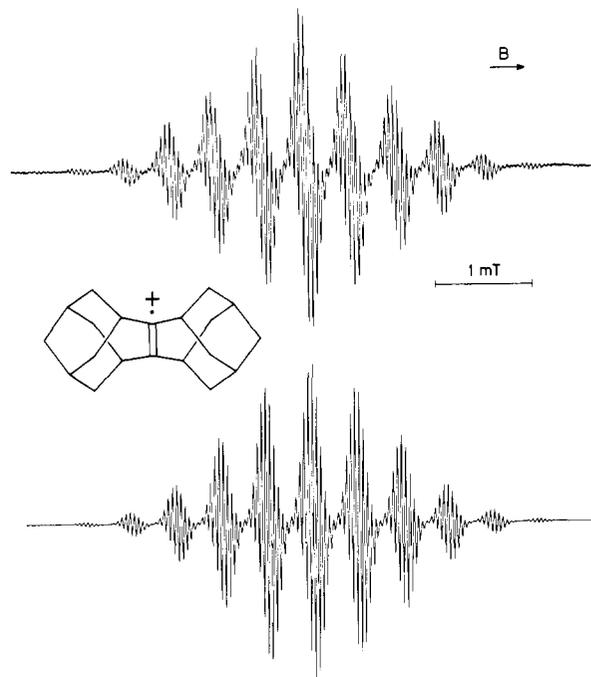


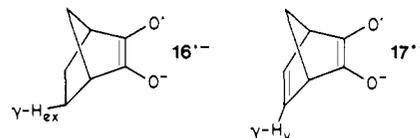
Figure 4. Top: ESR spectrum of 7^{2+} ; solvent, $CH_2Cl_2/CF_3COOH/(CF_3CO)_2O$ (10:1:1); counterion, CF_3COO^- ; temperature, 193 K. Bottom: simulation using coupling constants listed in Table II; line shape, Lorentzian, line width, 0.020 mT.

Table II. Proton Coupling Constants (millitesla) and g Factors for the Radical Cations of Adamantylideneadamantane (**5**), Isopropylideneadamantane (**6**), Sesquihomoadamantane (**7**), and Dimethylhomoadamantane (**8**)^a

| proton | 5^{2+} ^b | 6^{2+} | 7^{2+} | 8^{2+} |
|---------------|-----------------------|----------------|----------------|----------------|
| β | 0.058 (4 H) | 0.05 (2 H) | 0.043 (4 H) | 0.061 (2 H) |
| γ -eq | 0.327 (8 H) | 0.24 (4 H) | 0.486 (8 H) | 0.454 (4 H) |
| γ -ax | 0.047 (8 H) | 0.04 (4 H) | 0.043 (8 H) | 0.050 (4 H) |
| δ | 0.605 (4 H) | 0.71 (2 H) | 0.439 (4 H) | 0.645 (2 H) |
| ϵ | 0.012 (4 H) | <i>c</i> (2 H) | <i>c</i> (4 H) | <i>c</i> (2 H) |
| Me(β) | | 1.62 (6 H) | | 1.555 (6 H) |
| g | 2.0032 | 2.0029 | 2.0033 | 2.0030 |

^a Experimental error $\pm 1\%$ in the coupling constants (± 0.01 mT for 6^{2+}), ± 0.0001 in g . ^b Reference 15. ^c Not observed.

(0.311 mT) and 2^{2+} (0.353 mT) to $\gamma-H_v$ (0.064 mT) in 4^{2+} is consistent with the corresponding hyperfine data for $\gamma-H_{ex}$ (0.249 mT)²⁸ in the semidione 16^{2-} and $\gamma-H_v$ (0.070 mT)³² in its un-



saturated analogue 17^{2-} . The singly occupied orbital (SOMO) in these radical anions has nodal properties similar to those in 1^{2+} , 2^{2+} , and 4^{2+} , since it is symmetric with respect to the molecular mirror plane passing through the middle of the spin bearing π -system.³³

Table II gives the hyperfine data for 6^{2+} , 7^{2+} , and 8^{2+} . The assignment of protons in the individual positions is based on comparison with the corresponding values for 5^{2+} , which have all

(29) Kopecky, K. R.; Miller, A. J. *Can. J. Chem.* **1984**, *62*, 1840.

(30) The multiplet due to the exo protons appears downfield relative to that of the endo protons, because the latter are situated in the shielding cone of the π -bond.

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

(32) Blankespoor, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 6196.

(33) It is noteworthy that $\gamma-H_v$ in the radical cations of structurally related hydrazines have coupling constants comparable to those of $\gamma-H_{ex}$ in their saturated analogues. In these radical cations,³⁴ unlike 1^{2+} , 2^{2+} , and 4^{2+} , the SOMO (represented by a π^* -orbital of the N=N group) exhibits a nodal plane between the two spin-bearing atoms.

(34) Nelsen, S. F.; Frigo, T. B.; Kim, Y.; Thompson-Colón, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 7926.

(35) Nelsen, S. F.; Kapp, D. L.; Gerson, F.; Lopez, J. *J. Am. Chem. Soc.* **1986**, *108*, 1027.

been unequivocally assigned by specific deuterations.^{15,35} These values have also been included in Table II.

The coupling constants of β -H in $5^{+\cdot}-8^{+\cdot}$ (0.04–0.06 mT) are considerably smaller than the analogous values for $1^{+\cdot}$, $2^{+\cdot}$, and $4^{+\cdot}$, because in the former such protons lie much closer to the nodal plane of the olefinic π -system than in the latter (the dihedral angle θ in $5^{+\cdot}-8^{+\cdot}$ is almost 90°). The equatorial and axial positions of the γ -protons (γ -H_{eq} and γ -H_{ax}) in $5^{+\cdot}-8^{+\cdot}$ correspond to the exo and endo positions, respectively, in $1^{+\cdot}$ and $2^{+\cdot}$. The coupling constants of γ -H_{eq} (0.24–0.49 mT) in the former are thus of similar magnitude as those of γ -H_{ex} (0.31–0.36 mT) in the latter radical cations, and the same statement holds for the coupling constants of γ -H_{ax} (0.04–0.05 mT) with respect to those of γ -H_{en} (0.06–0.08 mT).

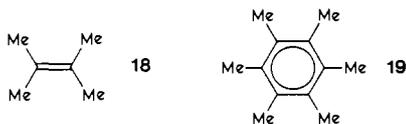
Spin Delocalization in the Radical Cations of Tetraalkyl-Substituted Ethenes. The question of how effective the large polycyclic groups are at delocalizing π -spin population in radical cations can be addressed semiquantitatively by employing the method of Fessenden and Schuler³⁶ and Fischer.³⁷ For alkyl-substituted neutral π -radicals, these authors have suggested the use of the following equations:

$$a(\text{H}[\text{Me}]) = Q[\text{Me}]\rho_s^\pi \quad (2)$$

$$\rho_s^\pi = \rho_0^\pi(1 - \Delta X[\text{R}_1])(1 - \Delta X[\text{R}_2]) \quad (3)$$

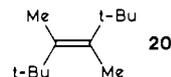
Equation 2 relates the coupling constant, $a(\text{H}[\text{Me}])$, of the three protons in a methyl substituent to the spin population, ρ_s^π , at the substituted carbon π -center; the proportionality factor $Q[\text{Me}]$ has been estimated as 2.5–3.2 mT for neutral radicals.^{36,37} In eq 3, ρ_0^π denotes the spin population at this center in the absence of delocalization into substituents, while $\Delta X[\text{R}]$ represents the fraction of ρ_0^π removed by the alkyl substituent R; a value $\Delta X[\text{Me}] = 0.081$ has been suggested for methyl-substituted neutral radicals.³⁷

We first apply eq 2 and 3 to the radical cations of tetramethylethene (**18**) and hexamethylbenzene (**19**), which have two



and six equivalent carbon π -centers, respectively. By setting $a(\text{H}[\text{Me}]) = 1.72$ mT³⁸ for $18^{+\cdot}$ ($\rho_0^\pi = 1/2$) and 0.645 mT³⁹ for $19^{+\cdot}$ ($\rho_0^\pi = 1/6$), four equations are obtained, two for each radical cation. The solution is $Q[\text{Me}] = 4.36$ mT and $\Delta X[\text{Me}] = 0.111$,⁴⁰ along with $\rho_s^\pi = 0.395$ for $18^{+\cdot}$ and 0.148 for $19^{+\cdot}$. The considerably larger values of $Q[\text{Me}]$ and $\Delta X[\text{Me}]$ for the radical cations than for the neutral species are consistent with the enhanced electron release from the methyl substituent to the positively charged carbon π -center.

Equations 2 and 3, in which $Q[\text{Me}] = 4.36$ mT and $\Delta X[\text{Me}] = 0.111$, are then used for the radical cation of dimethylhomoadamantene (**8**). With $\rho_0^\pi = 1/2$ and $a(\text{H}[\text{Me}]) = 1.555$ mT (Table II), the solution is $\rho_s^\pi = 0.357$ and $\Delta X[\text{Homoad}] = 0.197$. This ΔX value may be compared to $\Delta X[t\text{-Bu}] = 0.237$, which results from analogous calculations for the radical cation of *trans*-di-*t*-butyldimethylethene (**20**) with $a(\text{H}[\text{Me}]) = 1.48$ mT.^{23b} Expectedly, a tertiary alkyl substituent has a larger ΔX value than a secondary one.



In the case of the radical cation of isopropylideneadamantene (**6**), eq 2 and 3 with $Q[\text{Me}] = 4.36$ mT, $\Delta X[\text{Me}] = 0.111$, and $a(\text{H}[\text{Me}]) = 1.62$ mT (Table II) lead to the π -spin populations $\rho_s^\pi = 0.372$ and $\rho_0^\pi = 0.471$ at the dimethyl-substituted carbon center. This result leaves $\rho_0^\pi = 0.529$ for the carbon π -center in the adamantylidene moiety. Unfortunately, the π -spin population ρ_s^π at this center and the pertinent $\Delta X[\text{Ad}]$ value cannot be derived in that way without further information available. We estimate that $\Delta X[\text{Ad}]$ should be similar to $\Delta X[\text{Homoad}]$ and that ΔX values close to 0.2 are also expected for the bicyclic alkyl substituents in the radical cations of *anti*- and *syn*-sesquinorbornenes (**1** and **2**) and *syn*-sesquinorbornatriene (**4**).

Bending in $1^{+\cdot}$, $2^{+\cdot}$, and $4^{+\cdot}$. Dewar's semiempirical method, AM1,⁴¹ like its forerunners, has the great advantage that it is fast enough to be applied to compounds as large as those considered in this paper and not to models. It has been shown⁴² that, quite surprisingly, the coupling constants of both α - and β -protons in alkyl radicals and a variety of other simple radicals and radical ions are obtained to a reasonable accuracy, when the hydrogen 1s-spin populations, $\rho(\text{H})$, calculated with the use of AM1-UHFQ, are multiplied by an appropriate proportionality factor K . UHFQ here stands for the unrestricted Hartree-Fock (UHF) calculations that implement quartet (Q) annihilation⁴³ on the final function. To this aim, Bischof's subroutine,⁴⁴ which suffices for radicals without filled π -levels below formal SOMO, has been used.⁴²

In the case of $1^{+\cdot}$, $2^{+\cdot}$, and $4^{+\cdot}$, the energy surfaces calculated by AM1-UHFQ do not reveal any bending at the carbon atoms of the central double bond, as far as the equilibrium geometry is concerned. However, this result cannot be trusted, because the same method indicates that the neutral molecules **1**, **2**, and **4** should be essentially planar, at variance with the evidence from experiment (see the introduction). Although the energy-optimized structures are clearly not qualified for consideration of geometry at the olefinic carbon atoms in question, we may discuss the proton coupling constants for $1^{+\cdot}$, $2^{+\cdot}$, and $4^{+\cdot}$ as a function of the out-of-plane deformation angle ϕ at the carbon atoms of the central double bond.

Figure 5 shows the calculated 1s-spin populations $\rho(\beta\text{-H})$ and $\rho(\gamma\text{-H}_{\text{an}})$, at the β - and γ -anti-hydrogen atoms of $1^{+\cdot}$, $2^{+\cdot}$, and $4^{+\cdot}$ plotted versus ϕ . Positive and negative values of ϕ signify an endo and an exo bending, respectively, at the olefinic carbon π -center. It is evident that $\rho(\beta\text{-H})$ increase whereas $\rho(\gamma\text{-H}_{\text{an}})$ decrease with the enlargement of ϕ .

Prior to the discussion of the plot in Figure 5, it is important to note that the observed coupling constants are vibrationally averaged values over the energy surface which have rather a shallow form in radicals. In the particular case of $1^{+\cdot}$, this statement means that positive and negative values of ϕ will average to zero for reasons of symmetry. The angle $\phi = 0^\circ$ in $1^{+\cdot}$ corresponds in Figure 5 to the calculated spin population $\rho(\beta\text{-H}) = 2.97 \times 10^{-3}$ from which a proportionality factor $K_\beta = 109.8$ mT is obtained with use of the experimental coupling constant $a(\beta\text{-H}) = 0.326$ mT. This value of K_β compares well with that obtained previously (117.7 mT)⁴² for several simple radicals and radical ions. When the coupling constants $a(\beta\text{-H})$ of 0.392 and 0.252 mT, observed for $2^{+\cdot}$ and $4^{+\cdot}$, respectively, are divided by 109.8 mT, they yield $\rho(\beta\text{-H}) = 3.57 \times 10^{-3}$ in $2^{+\cdot}$ and 2.30×10^{-3} in $4^{+\cdot}$. These spin populations correspond in Figure 5 to $\phi = +7^\circ$ in the former and $+14^\circ$ in the latter radical cation.

An analogous procedure can be applied to the coupling constants $a(\gamma\text{-H}_{\text{an}})$. First, a proportionality factor, $K_\gamma = 324$ mT, is derived from the experimental value $a(\gamma\text{-H}_{\text{an}}) = 1.346$ mT for $1^{+\cdot}$ and the spin population $\rho(\gamma\text{-H}_{\text{an}}) = 4.15 \times 10^{-3}$ calculated for $\phi =$

(36) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.

(37) Fischer, H. Z. *Naturforsch. A* **1965**, *20*, 428.

(38) Shida, T.; Egawa, Y.; Kubodera, H.; Kato, T. *J. Chem. Phys.* **1980**, *73*, 5963.

(39) Dessau, R. M.; Shih, S.; Haiba, E. I. *J. Am. Chem. Soc.* **1970**, *92*, 412.

(40) Use of $\Delta X[\text{Me}] = 0.111$ and $Q[\text{Me}] = 4.36$ mT is only semiquantitative, and different values may be appropriate for radical cations of ethenes with fewer alkyl substituents. For instance, the radical cation of *trans*-2-butene has $a(\text{H}[\text{Me}]) = 2.39$ mT, so that $Q[\text{Me}]$ as large as 5.38 mT is required if $\Delta X[\text{Me}] = 0.111$.

(41) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(42) Nelsen, S. F. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1005.

(43) Amos, T.; Snyder, L. C. *J. Chem. Phys.* **1964**, *41*, 1773.

(44) Bischof, P. *J. Am. Chem. Soc.* **1976**, *98*, 6844.

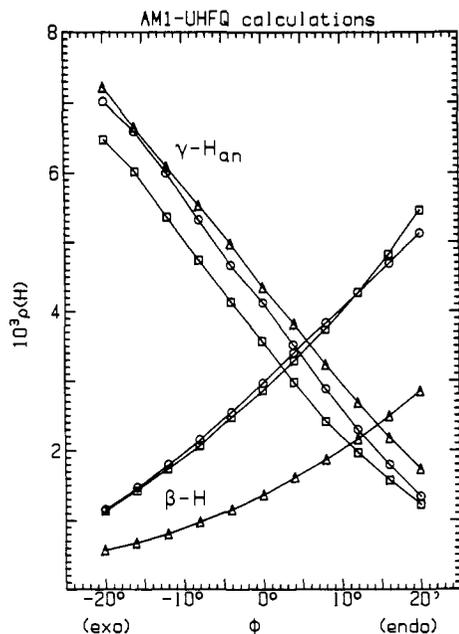


Figure 5. 1s-spin populations, $\rho(H)$, calculated by AM1-UHFQ for the β - and γ -anti-hydrogen atoms (β -H and γ -H_{an}) in $1^{+\bullet}$ (circles), $2^{+\bullet}$ (squares), and $4^{+\bullet}$ (triangles) as a function of the out-of-plane deformation angle ϕ at the carbon atoms of the central double bond.

0° in this radical cation (Figure 5). The factor K_γ is then used to convert the coupling constants $a(\gamma\text{-H}_{an})$ of 0.746 and 1.066 mT, observed for $2^{+\bullet}$ and $4^{+\bullet}$, into $\rho(\gamma\text{-H}_{an})$ 2.30×10^{-3} and 3.29×10^{-3} , respectively. The angles corresponding to these spin populations in Figure 5 are $+8^\circ$ for $2^{+\bullet}$ and $+7^\circ$ for $4^{+\bullet}$.

The coupling constants $a(\beta\text{-H})$ and $a(\gamma\text{-H}_{an})$ for $2^{+\bullet}$ thus strongly suggest that this radical cation is bent by an angle ϕ of $7\text{--}8^\circ$, which is significantly smaller than that ($15.5\text{--}18^\circ$) found for derivatives of the neutral compounds **2** (see the introduction). According to the analogous proton hyperfine data for $4^{+\bullet}$, its angle ϕ should be in the range $7\text{--}14^\circ$. The radical cation $4^{+\bullet}$ appears, therefore, to be more strongly bent than its monoene counterpart $2^{+\bullet}$, again in line with the results of X-ray crystallography,^{13c} which indicate that derivatives of **4** are more pyramidal than those of **2**. It is important to note that ϕ turns out to be positive, i.e., the bending in $2^{+\bullet}$ and $4^{+\bullet}$ is endo as in the neutral diamagnetic compounds and not exo as in the excited triplet state of **2**,¹² which also has singly occupied π -orbitals.

Ease of Electron Removal. The photoelectron (PE) spectra of **1** and **2** were reported by Brown and co-workers^{45a} and by Houk and co-workers,^{45b} and both groups ran some model compounds for an interpretation of the observed vertical ionization potentials (vIP). The only other extensive set of ionization potentials (IP) measured for tetraalkylalkenes by PE spectroscopy is that of Grosjean and co-workers,⁴⁶ who reported unusually precise values for 12 n -alkyl-substituted compounds but did not state how these data were extracted from the spectra. One of us⁴⁷ has pointed out that an "alkyl-group inductive parameter", $n(\text{eff})$ derived from PE spectra is useful in considering the changes of vIP values by an alkyl substitution. A plot of the above-mentioned PE data^{45,46} versus the sum of the $n(\text{eff})$ values⁴⁷ for the four attached alkyl groups is shown in Figure 6. (The correlation of IP with $n(\text{eff})$ is similar in concept to that with the number of carbon atoms that has been employed by Brown and co-workers.^{45a} However, we believe that use of $n(\text{eff})$ instead of such a number represents a significant improvement, because the connectivity of the carbon

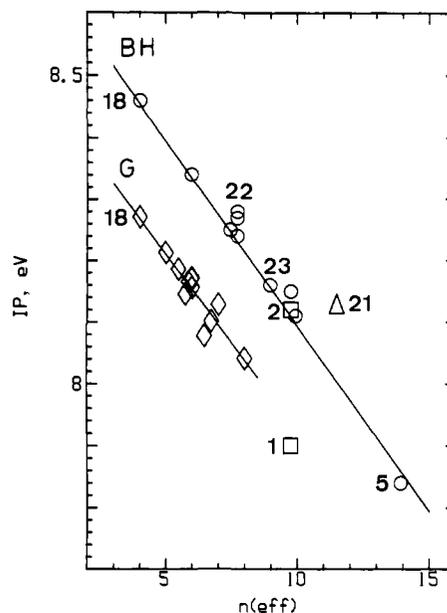


Figure 6. Ionization potentials (IP) of alkyl-substituted tetraalkylethenes plotted versus summed $n(\text{eff})$ values. Lozenges with regression line G are from ref 46 [**18**, EtMeC=CMe₂, n -PrMeC=CMe₂, i -PrMeC=CMe₂, n -BuMeC=CMe₂, Z-EtMeC=CMeEt, E-EtMeC=CMeEt, E-EtMeC=CMe- n -Pr, Et₂C=CMe₂, n -BuEtC=CMe₂, Et₂C=CMeEt, Et₂C=CMeEt]. Circles with regression line BH are from ref 45a [**23**, isopropylidene-cyclopentane, bicyclo[5.3.0]dec-1,7-ene, 3-methyltricyclo[6.2.1.0^{2,7}]undec-2,7-ene, 4,5-dipropyl-oct-4-ene] and ref 45b [**5**, **18**, **22**, Z- and E-2,3,4,5-tetramethylhex-3-ene]. Squares are from ref 45a [**1**, **2**] and the triangle is from ref 45b [**21**].

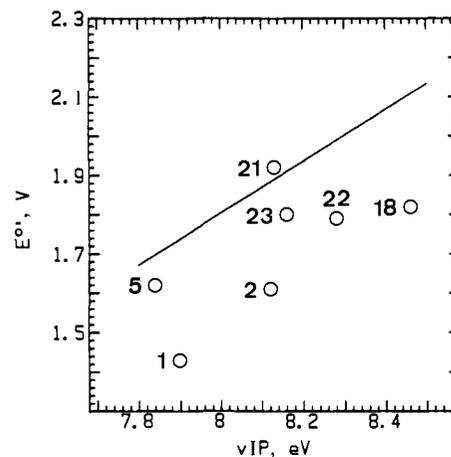


Figure 7. Plot of oxidation potentials E° in solution versus vertical ionization potentials (vIP) for several tetraalkylethenes. See text for the meaning of the line drawn, which is not a regression line involving these data.

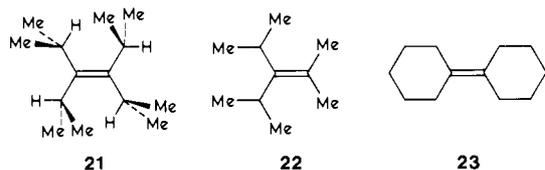
atoms does matter some.) The data of Grosjean (lozenges in Figure 6) follow $n(\text{eff})$ with a correlation coefficient of 0.940, a slope of -0.057 , and an intercept of 8.50 eV; the average deviation from the pertinent regression line (G) is only 0.013 eV. There is clearly a shift of this line (about 0.13 eV) relative to the second, almost parallel regression line (BH) derived by the use of 10 vIP values (circles in Figure 6) that were selected from Brown and Houk's work⁴⁵ (acyclic, five- to seven-membered ring cyclic, and polycyclic compounds). These values include **22** and **23**⁴⁸ but exclude **1**, and **2** (squares in Figure 6) as well as **21** (triangle). They follow $n(\text{eff})$ with a correlation coefficient of 0.992, a slope of -0.062 , and an intercept of 8.73 eV; the average deviation is 0.016 eV (which is within the experimental error). The shift of the line G relative to BH may be due to the fact that Grosjean's

(45) (a) Brown, R. S.; Buschek, J. M.; Kopecky, K. R.; Miller, A. J. *J. Org. Chem.* **1983**, *48*, 3692. (b) Mollere, P. D.; Houk, K. N.; Bomse, D. S.; Morton, T. H. *J. Am. Chem. Soc.* **1976**, *98*, 4732.

(46) Masclet, P.; Grosjean, D.; Mouvier, G.; Dubois, J. *J. Electron. Spectrosc.* **1973**, *2*, 225.

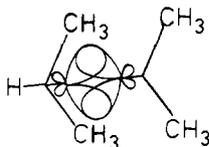
(47) (a) Nelsen, S. F. *J. Org. Chem.* **1984**, *49*, 1891. (b) Values of $n(\text{eff})$ were determined from PE measurements on alkyl halides.

(48) (a) Langler, R. F.; Tidwell, T. T. *Tetrahedron Lett.* **1975**, 777. (b) Bomse, D. S.; Morton, T. H. *Ibid.* **1975**, 781.



data refer not to vIP but to adiabatic ionization potentials (aIP).

Of the three vIP values (**1**, **2**, and **21**) not used for the derivation of the line BH, that of *syn*-sesquiorbornene (**2**) lies on this line, despite a considerable endo pyramidalization at the olefinic carbon atoms. By contrast, the corresponding potential of the anti isomer **1**, which should be more planar at the double bond, is lower by 0.22 eV (5.1 kcal/mol) and thus falls by the same amount below the line BH. Both Brown and co-workers^{45a} and Houk and co-workers¹⁰ discuss the pyramidalization of **2** relative to **1**. They agree that bending in **2** occurs because it relieves eclipsing interactions between vicinal allylic σ (C-C) bond electrons and those in the π -system. Less pyramidalization in **1** is rationalized by the argument that, in this case, such interactions would not be significantly relieved by bending; a relief on one side of the C=C bond is opposed by an increased strain on the other. Since **1** retains the vicinal allylic σ (C-C), π -destabilization, it is significantly easier to remove an electron from **1** than from **2**. We do point out, however, that the vIP- σ,π interaction story may be more complicated than the above discussion implies. In this context, it is noteworthy that the vIP value of tetraisopropylethene (**21**) lies 0.12 eV (2.8 kcal/mol) above the line BH, whereas the potentials of the three isomeric diisopropyldimethylethenes, employed in the derivation of this line (circles at $n(\text{eff}) = 7.4$), exhibit no unusual features. The compound **21** exists in the conformation shown in its formula above.⁴⁸ In addition, a view of **21** from below this formula is given as follows:



The two back isopropyl substituents and the C-H bond of the right-hand isopropyl group have been omitted for clarity and the C=C bond is presented in the banana shape (see, e.g., ref 10). It may be noted that the π -orbitals of the double bond are eclipsed with the left-hand isopropyl group but staggered with the right-hand one. An analogous consideration applied to **1**, **2**, and **5** reveals that all four branched alkyl groups are eclipsed in **1** and **2** but staggered in **5**. We thus believe that substantially more data have to be obtained to fully elucidate the reasons why the values for **1** and **21** deviate in different direction from the line BH determined by the data for other alkenes (Figure 6). Presumably, σ^*,π - as well as σ,π -mixing would need to be considered for a more detailed understanding of how vIP values change with alkyl substitution and orientation relative to the π -orbital.

As discussed in the introduction, **2** is significantly more pyramidal than **1** at the carbon atoms of the double bond. Furthermore, the ESR data indicate that the bending at these atoms is less for **2**⁺ than for **2**. If **2** flattened upon electron removal but **1** remained planar, one would expect that the relaxation energy upon ionization should be greater for **2** than for **1**. However, this is experimentally not the case. Table III includes vIP data and the cyclic-voltammetric oxidation potentials $E^{\circ'}$ of those compounds for which both values have been measured. It is evident that **1** is by 0.18 eV easier to oxidize in solution than **2**, while the gas-phase vIP value of **1** is 0.22 eV lower than that of **2**. These experimental results point to similar relaxation energies of the two isomers. Figure 7 presents a plot of $E^{\circ'}$ versus vIP for the compounds listed in Table III. The regression line shown is the one determined for fused-ring aromatic hydrocarbons, alkyl derivatives of benzene, and bicyclic peroxides; their data lie on this line with a scatter of 0.1 eV (2 kcal/mol).⁴⁹ Compounds such

Table III. Vertical Ionization Potentials (vIP in electronvolts) from Photoelectron Spectra and Cyclic Voltammetric Oxidation Potentials ($E^{\circ'}$ in volts) for Tetraalkylethenes **1**, **2**, **5**, **18**, **21**, **22**, and **23**

| | 1 | 2 | 5 | 18 | 21 | 22 | 23 |
|---------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| vIP | 7.90 ^a | 8.12 ^a | 7.84 ^b | 8.46 ^b | 8.13 ^b | 8.28 ^c | 8.16 ^a |
| $E^{\circ'}$ ^d | 1.43 ^e | 1.61 ^e | 1.62 ^e | 1.82 ^f | 1.92 ^f | 1.79 ^f | 1.80 ^f |

^aReference 45a. ^bReference 45b. ^cSee ref 45b. ^dConditions: 2 mM olefin in 0.1 M Bu₄BF₄ in 20:1:1 CH₂Cl₂/TFA/TFAA at Pt; 0.2 V/s scan rate. ^eReference 20. ^fThis work.

as hydrazines and hydroxylamines, which have larger relaxation energies upon electron removal than those used for the regression, lie below the line. Since $E^{\circ'}$ include solvation energies, we do not doubt that the negative deviations of the less branched alkenes **18**, **22**, and **23** from the regression line are partially caused by better solvation of their radical cations relative to the tetra- α -branched alkenes **1**, **2**, **5**, and **21**. Both isomers **1** and **2** lie about the same distance below the line, 0.31 eV (7.1 kcal/mol) for **1**, and 0.27 eV (6.2 kcal/mol) for **2**, while for **5** such a lowering is only 0.08 eV (1.8 kcal/mol) and even less for **21**. It is difficult to rationalize the similar relaxation energies for **1** and **2**, unless both isomers undergo significant changes in geometry upon ionization. Perhaps, in contrast to **2**, which flattens on passing to **2**⁺, the increase of the C=C bond length upon electron removal makes **1**⁺ more pyramidal at the olefinic carbon atoms than **1**.

Experimental Section

2,3-exo,exo-Dideuterio-anti-sesquiorbornene (1-d₂). A total of 5.00 g of a 3.8:1 mixture of unsaturated anhydrides **13** and **14** (21.7 mmol)²⁹ was dissolved in 150 mL of EtOAc, 0.30 g of PtO₂ added, and the mixture treated with D₂ until uptake ceased and the catalyst coagulated. After filtration through Celite, solvent removal gave 5.05 g (quantitative yield) of the deuterated, saturated anhydrides. Repetition on a 1.00-g scale led to similar results. The mixture of deuterated anhydrides (6.00 g, 25.6 mmol) was heated to 80 °C in 75 mL of EtOH, 25 mL of H₂O, and 4.0 g of KOH (71.3 mmol) for 2 h. After cooling, solvent evaporation gave an orange residue, which was dissolved in 100 mL of water, filtered, and acidified with HCl. The precipitate was extracted into EtOAc, dried (Na₂SO₄), and concentrated to a brown solid. Recrystallization from EtOAc/hexane gave 2.5 g of deuterated *anti*-sesquiorbornane dicarboxylate (39%). ¹H NMR (CD₃CN) δ 2.65 (br s, 2 H), 2.53 (br s, 2 H), 2.06 (m, 3 H), 1.90 (br d, $J = 11.4$ Hz, 1 H), 1.56 (m, 2 H), 1.31 (m, 2 H), 1.21 (br d, $J = 10.1$ Hz, 1 H), 1.06 (br d, $J = 11.4$ Hz, 1 H). This diacid (2.00 g, 7.93 mmol) in 125 mL of benzene was treated with 9.0 g of Pb(OAc)₄ (20 mmol), and the suspension stirred until the mixture became homogeneous (about 30 min), while N₂ was passed through the solution by using a gas-dispersion tube. CaCl₂ (1.0 g, 24 mmol) was added, and the mixture heated to reflux, causing a vigorous evolution of gas and formation of a white precipitate. After refluxing for 8 h, cooling, filtration, and evaporation, the filter cake was washed with CH₂Cl₂, and the washes were used to dissolve the residue. Treatment of the CH₂Cl₂ solution with 10% HClO₄ gave a red-brown precipitate, which was removed by filtration. Further washing with 10% HClO₄, H₂O, drying with MgSO₄, filtration, and evaporation yielded 0.78 g of crude product as an oil. This oil was dissolved in 5 mL of quinoline, treated with 0.25 g of copper powder, and refluxed 1 h. After cooling to room temperature and dilution with ether, the solution was extracted several times with 10% HCl and aq Na₂CO₃, dried with MgSO₄, filtered, and evaporated to a brown oil. TLC mesh column chromatography (100 g of silica gel/hexane) gave 550 mg of pure **1-d₂** (43%), mp 63–64 °C. Empirical formula C₁₂H₁₄D₂ was established by high-resolution mass spectrometry. ¹H NMR (CDCl₃) δ 2.83 (br s, 4 H), 1.69 (m, 2 H), 1.30 (m, 4 H), 1.11 (m, 4 H). Integration of the NMR indicated 100% deuterium incorporation.

2-exo-Deuterio-syn-sesquiorbornene (2-d). To 600 mg of Na (26.1 mmol, 8.7 eq.) was injected 0.7 mL of Hg by syringe, and after a few moments, the 6% Na amalgam formed exothermically. CH₃OD (30 mL) and Na₂DPO₄ (3.3 g, 23.2 mmol, 7.7 equiv) were added, and the suspension was stirred 30 min. Subsequently, 900 mg of **15** (3.00 mmol)^{11c}

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in tetrahydrofuran was added by cannula, and the mixture stirred 4 days. After quenching with 50 mL of H₂O, the mixture was extracted with 40 mL of pentane. The organic phase was washed with 3 × 70-mL portions of H₂O, dried (MgSO₄), and filtered through basic alumina. Evaporation gave 0.42 g of **2-d** as a waxy solid, which was sublimed (35 °C, 0.3 Torr, coldfinger cooled with dry ice) to give material, mp 32–33 °C. ¹H NMR (CDCl₃) δ 2.96 (br s, 4 H), 1.53 (m, ca. 3 H), 1.36 (br d, *J* = 8.0 Hz, 2 H), 1.04 (d, *J* = 8.0 Hz, 2 H), 0.83 (m, 4 H). ¹³C NMR (CDCl₃) δ 151.44 (C), 50.19 (CH₂), 42.80 (CH), 25.24 (CH₂), 24.90 (CD, *t*, *J* =

19.5 Hz). Integration of the ¹H NMR spectrum indicated 82% D incorporation.

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¹³C NMR and X-ray Structure Determination of 1-(Arylazo)-2-naphthols. Intramolecular Proton Transfer between Nitrogen and Oxygen Atoms in the Solid State

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Abstract: The tautomeric reaction involving a single proton transfer in 1-(phenylazo)-2-naphthol and its 4'-methoxy, ethoxy, and *N,N*-dimethylamino derivatives has been investigated with variable-temperature solution and high-resolution solid-state ¹³C NMR spectroscopy. Crystal structures of the parent unsubstituted compound and the 4'-*N,N*-dimethylamino derivative have been determined. All of these compounds undergo a fast proton exchange on the NMR time scale between the tautomeric azo and hydrazone forms in both solution and the crystalline phase. Equilibrium compositions in the solid materials are similar to those measured in solution. Crystals of 1-(phenylazo)-2-naphthol are monoclinic, *a* = 27.875 (7), *b* = 6.028 (2), *c* = 14.928 (5) Å, β = 103.57 (2)°, the space group is *C2/c* with *Z* = 8, and the structure at 213 K was refined to an *R* factor of 0.0414 on 1082 observed reflections. Crystals of 1-([4'-(dimethylamino)phenyl]azo)-2-naphthol are monoclinic, *a* = 7.604 (1), *b* = 7.970 (3), *c* = 24.381 (7) Å, β = 99.33 (2)°, the space group is *P2₁/c* with *Z* = 4, and the structure at 193 K was refined to an *R* factor of 0.0405 on 1522 observed reflections.

Hydrogen-bonded systems, both in solution and in the solid phase, have attracted considerable attention over the years.¹⁻³ Especially interesting are those structures where hydrogens are transferred in a tautomeric change.^{4,5} In the solid state, such proton transfers take place in an environment where packing forces may appreciably affect the dynamics of the reaction as well as the tautomeric composition.⁶⁻⁹ A knowledge of these processes is fundamental to an understanding of the structure and behavior of such solids and could also have technological implications, as proton exchanges in solids have potential utility as the basis of optical data storage devices.¹⁰⁻¹²

This tautomeric behavior in solution has been recognized in a number of azo dyes.^{13,14} Intramolecular proton transfers between nitrogen and oxygen atoms have been studied by various techniques, including visible spectrophotometry¹⁵ and NMR spectroscopy.¹⁶⁻²⁵ The latter method has provided a quantitative measure of the relative amounts of the azo and hydrazone forms present in the equilibrium. In CDCl₃ solution at room temperature, 1-(phenylazo)-2-naphthol (**1**) has been found to exist as a rapidly exchanging mixture of ca. 70% of the hydrazone form

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