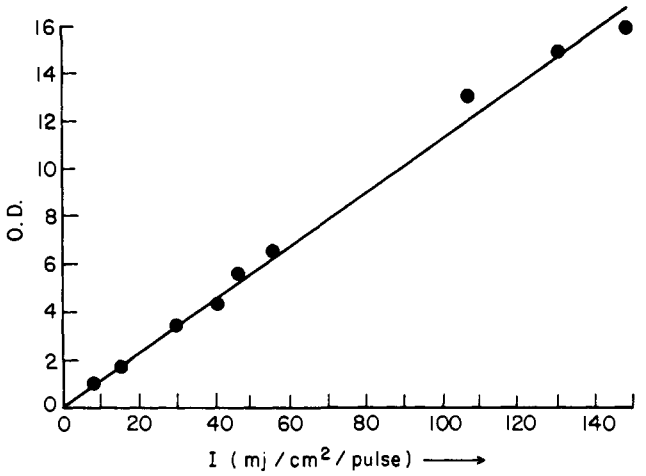

Figure 1. Dependence of photoionization yield of aminoperylene in NaLS on the laser intensity.

by green light. Several other molecules, tetramethylbenzidine,[7] phenothiazine,[8] etc., exhibit this unique effect, i.e., a substantial reduction in their photoionization potentials in NaLS micelles compared with the gas phase. Aminoperylene falls into this category and is quite unlike molecules such as pyrene, anthracene, etc., which follow two-photon photoionization in these systems. The difference in behavior is due to the location of the molecule in the micelle and hence its local micellar environment.[9]

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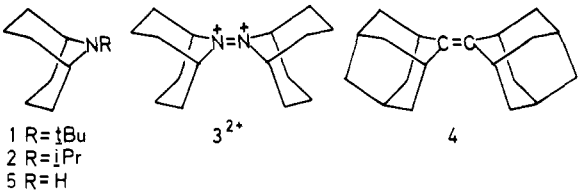
Adamantylideneadamantane Radical Cation, a Long-Lived One-Electron, Two-Center π-Bonded Species

Sir:

Simple trialkylamine cations have very short lifetimes in neutral or basic solutions, but are increasingly longer lived in more acidic solutions.[1] The only reason for short lifetimes in the absence of acid seems to be rapid deprotonation at carbons adjacent to nitrogen, because, when such C–H bonds are forced by bicyclic rings to be perpendicular to the N-centered p orbital in the cation, considerably longer lifetimes result. Thus 9-*tert*-butyl-9-azabicyclo[3.3.1]nonane cation radical (**1**$^{+}\cdot$) lasts over an hour in acetonitrile, under conditions where its *N*-isopropyl analogue **2**$^{+}\cdot$ has a submillisecond lifetime like other trialkylamine radical cations.[2] This Bredt's rule stabilization of cationic trisubstituted nitrogen species even extends to the hydrazine dication **3**$^{2+}$, which has a lifetime of at least seconds,[3] in contrast to the submillisecond lifetime for the dicat-



ions of all hydrazines studied which lack Bredt's rule stabilization of hydrogens on carbons attached to nitrogen. Given these results, we suspected that adamantylideneadamantane (**4**) might be reversibly oxidized to **4**$^{+}\cdot$ and provide the first example of a long-lived monoolefin cation radical (a "one-electron π bond"). This proves to be the case.

The cyclic voltammogram of **4** in acetonitrile shows an electrochemically reversible one-electron oxidation wave $E^{\circ\prime}$ = 1.45 V vs. SCE, even at 10-mV/s scan rates, requiring a lifetime of at least seconds for **4**$^{+}\cdot$. Electrolytic oxidation in an ESR cell generates an air-sensitive radical, g = 2.0031, having a broadened multiplet for many hydrogens with a 3.0-G splitting constant, which we attribute to **4**$^{+}\cdot$. The best model available for the proton splittings expected for **4**$^{+}\cdot$ is **5**$^{+}\cdot$, which was generated by photolysis of the *N*-chloro compound in trifluoroacetic acid, analogously to other dialkylamine radical cations.[4] The complex ESR spectrum of **5**$^{+}\cdot$ was analyzed to give splittings a(1 H) = 19.8_4, a(N) = 17.3_4, a(8 H) = 3.9_6, a(2 H) = 0.9_9, g = 2.0034. We attribute the eight hydrogen splitting to the two sets of four hydrogens on C_2, C_4, C_6, and C_8. The C_1C_2, C_1C_8, C_5C_4, and C_5C_6 bonds are held in excellent geometry for hyperconjugation with the half-filled p orbital on nitrogen and each pair of geometrically inequivalent methylene hydrogens is equivalently disposed with respect to one of these CC bonds. We presume that the rather large equal splittings for the two sets of four equivalent hydrogens γ to the formal spin-bearing orbital are a result of dominant spin polarization from hyperconjugation-generated spin at C_2, C_4, C_6, and C_8. By analogy one expects **4**$^{+}\cdot$ to have a fairly large splitting for sixteen γ hydrogens, consistent with the ESR spectrum observed upon oxidation of **4**. Hyperconjugation in **4**$^{+}\cdot$ is apparently significantly more efficient at delocalizing spin to the γ carbons than in **5**$^{+}\cdot$, because $a(H_\gamma)$ for **4**$^{+}\cdot$ is ~50% larger than half $a(H_\gamma)$ for **5**$^{+}\cdot$. This effect could well be a result of a closer matching of the CC σ-bond energy with that of the carbon-centered π system of **4**$^{+}\cdot$ than with the nitrogen-centered p orbital of **5**$^{+}\cdot$. The positive "hole" of **4**$^{+}\cdot$ is for a bonding electron, while that of **5**$^{+}\cdot$ is formally (although not actually completely) nonbonding. Another piece of evidence which points to unusually important σ,π interaction in **4**$^{+}\cdot$ is provided by its g factor, which is higher than for other hydrocarbon radicals; $\Delta g = g - g_e$ is 8×10^{-4} for **4**$^{+}\cdot$, compared with the range of $2\text{–}4 \times 10^{-4}$ for polycyclic aromatic[5] and hexaalkylbenzene[6] cation radicals. The smaller π system for **4**$^{+}\cdot$ should lower Δg slightly according to the Stone equation,[5,7] the opposite direction to the experimental observation. An unusually low energy $\sigma \rightarrow \pi$ transition has been predicted to increase Δg.[8]

The $E^{\circ\prime}$ value of 1.45 V for **4**/**4**$^{+}\cdot$ might be thought surprisingly low compared with the range of 2.27–3.20 V for irreversible $E_{1/2}$ values of ethylene and mono- and dialkyl olefins.[9] It is thermodynamically as easy to remove an electron in solution from the two-electron π system of **4** as it is from the eighteen-electron π system of benzanthracene. Miller and co-workers[9] have emphasized a linear relationship between the vapor phase ionization potential and the solution phase oxidation potential for many types of compounds. Such a line can now be established employing thermodynamically significant $E^{\circ\prime}$ values for polycyclic aromatic hydrocarbons in acetonitrile, using the electrochemical data of Parker[10] and vertical ionization potentials determined by photoelectron spectroscopy,

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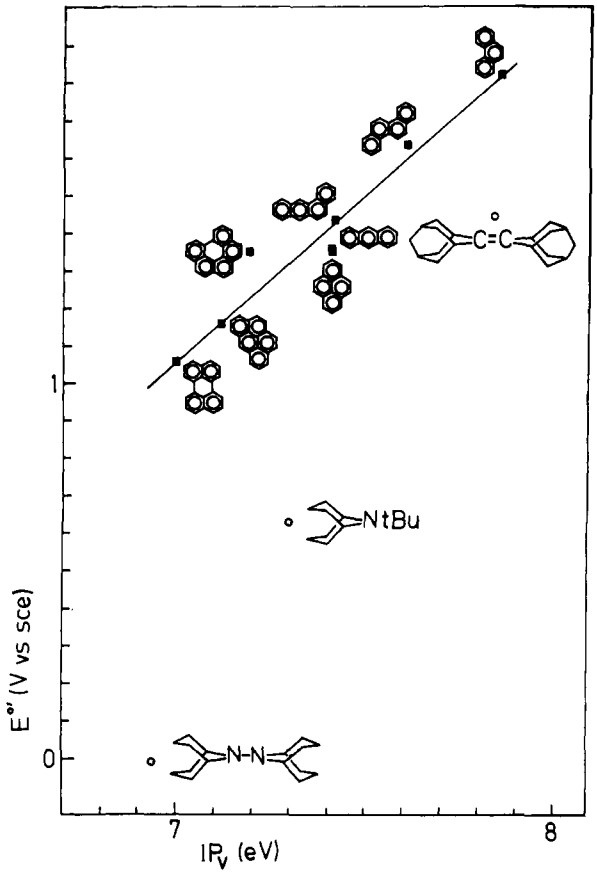

Figure 1. Plot of $E^{\circ\prime}$ (V vs. SCE in CH_3CN) vs. IP_v (eV) for fused aromatic hydrocarbons, compared with **1**, **3**, and **4**.

giving $E^{\circ\prime} = -5.21 + 0.89_5\ (IP_v)$.[11] There is a large lowering of IP_v for substitution of methyl for hydrogen of olefins (ethylene, 10.51 eV; tetramethylethylene, 8.42 eV[12]) and the additional lowering observed when alkyl groups are lengthened makes the observed IP_v for **4** of 7.84 eV not at all surprising.[13] $E^{\circ\prime}$ for **4**–$\mathbf{5}^{+\bullet}$ is approximately −0.36 V (8.3 kcal/mol below the aromatic hydrocarbon line), as shown graphically in Figure 1. The far smaller π system of $\mathbf{4}^{+\bullet}$ and its aliphatic substituents are expected to make solvent stabilization of $\mathbf{4}^{+\bullet}$ substantially different from that for the fused aromatic hydrocarbons used to determine the line shown. It is thermodynamically significantly easier to remove lone-pair electrons from **3** ($E^{\circ\prime}$ = −0.01 V,[3] vertical deviation from the hydrocarbon line −1.01 V) and **1** ($E^{\circ\prime}$ = +0.63 V,[1] vertical deviation −0.69 V), much more so than IP_v differences would suggest. Although solvation differences among **1**, **3**, and **4** cannot be ignored, we suggest that the most significant factor is the large rehybridization at nitrogen which occurs upon electron removal from **3**[14] and **1**; comparable rehybridization will not occur for **4**, which is already sp^2 hybridized at the vinyl carbons.

A particularly significant difference between the oxidation behavior of **3** and **4** involves removal of a second electron. The second oxidation wave in the CV of **3** is electrochemically reversible, and $E^{\circ\prime}_2 - E^{\circ\prime}_1$ is 1.19 V, the largest value yet reported for a compound showing two reversible electron transfers.[3] In contrast, **4** in acetonitrile shows a completely irreversible second oxidation wave peaking at +1.96 V (scan rate 100 mV/s), only 0.51 V positive of $E^{\circ\prime}_1$. Although the $\mathbf{3}^{+\bullet}/\mathbf{3}^{2+}$ and $\mathbf{4}^{+\bullet}/\mathbf{4}^{2+}$ couples have the same charge and similar alkyl group structures (we presume the remote methylenes of **4** are relatively unimportant), they are not isoelectronic. The third, antibonding π electron of $\mathbf{3}^{+\bullet}$ is reversibly removable, but the single π electron of $\mathbf{4}^{+\bullet}$ should be strongly bonding. Because of the small difference in potentials at which a second electron is removed from **4**, we suggest that the carbon-centered two-atom π dication which would be the hydrocarbon analogue of $\mathbf{3}^{2+}$ may not be formed and that the second electron removed may well be a σ electron which would be expected to cause rapid deprotonation and hence be irreversible, by analogy to the behavior of adamantane upon electrochemical oxidation.[15,16]

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Tetradecaisopropoxydihydridotetratungsten(IV). Oxidative Addition of PrO–H across a Tungsten-to-Tungsten Triple Bond

Sir:

Bimetallic compounds containing metal-to-metal multiple bonds[1] will occupy an important position in the development of transition metal cluster chemistry.[2] They are the smallest examples of unsaturated cluster compounds and should provide building blocks for the synthesis of new polynuclear cluster compounds. Furthermore their reactions should complement those well documented in mononuclear transition metal chemistry.[3] We now report the preparation and characterization of a novel tetranuclear tungsten compound which illustrates these considerations.

Hydrocarbon solutions of $W_2(NMe_2)_6(W{\equiv}W)$[4] react rapidly with 2-propanol at room temperature with the liberation of amine. Upon removal of the solvent a black solid of empirical formula $W(OPr^i)_3$ based on elemental analysis[5] was obtained. The black substance gave very complex NMR spectra and was thermally unstable yielding propylene, 2-propanol, and traces of water as volatiles when heated above 80 °C in vacuo. These observations contrast with the reaction between $Mo_2(NMe_2)_6$ and 2-propanol which yields the thermally stable and well-characterized compound $Mo_2(OPr^i)_6(Mo{\equiv}Mo)$.[6] Additional study of the reaction between $W_2(NMe_2)_6$ and 2-propanol in a sealed system showed that along with dimethylamine a gas noncondensable in liquid N_2 was formed. The latter was identified as molecular hydrogen by mass spectroscopy. The solids obtained from the reaction between $W_2(NMe_2)_6$ and 2-propanol are extremely soluble

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