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PROTON-DRIVEN DIELS–ALDER REACTION OF AZO COMPOUNDS WITH CYCLIC DIENES

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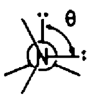
Abstract—Diels–Alder addition of bicyclic azo compounds to cyclic dienes would produce bis-N,N'-bicyclic hydrazines, but this reaction proves to be endothermic. The greater basicity of the adduct than of the azo compound makes the addition reaction 13.6–14.1 kcal mol^{-1} less endothermic (in water) if the protonated azo compound is employed instead of the neutral compound, and the addition reactions proceed well in acetonitrile if $HBF_4 \cdot Et_2O$ is used to protonate the azo compound before adding the diene. Preparations of the neutral hydrazines derived from 2,3-diazabicyclo[2.2.2]oct-2-ene (**5**) with 1,3-cyclohexadiene (**6**) and from 2,3-diazabicyclo[2.2.1]hept-2-ene (**10**) with **6** and 1,3-cycloheptadiene (**7**, **11**, and **13**, respectively) as well as the saturated hydrazines derived by catalytic hydrogenation (**9**, **12**, and **14**, respectively) are reported. The neutral adduct of **10**H$^+$ and cyclopentadiene, **15**, proves to be too thermally unstable for isolation, and the saturated form, **16**, is prepared by diimide reduction of **15**H$^+$. The neutral hydrazines all give radical cations and dications with appreciable solution lifetimes, and $\mathbf{9}^{2+}(BF_4^-)_2$ is the first isolable hydrazine dication. The thermodynamics of electron loss for these hydrazines are studied by cyclic voltammetry, and prove to be dominated by non-bonded steric interactions between the alkyl groups. Compound **9** is the most easily oxidized hydrazine known, at $E°' = -0.54$ V vs SCE.

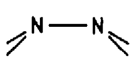
The tetraalkylhydrazine–tetraalkylhydrazine cation radical electron transfer equilibrium of Eq. (1) is

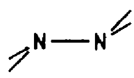
$$R_2\ddot{N}-\ddot{N}R_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} R_2\overset{\cdot\cdot}{N}\overset{+}{-}\dot{N}R_2 \qquad (1)$$

remarkably sensitive to the alkyl groups attached to nitrogen, especially when they are linked into rings.[1] Changes in the ring sizes change the shape of the molecule near the nitrogens, which is very important for the electron transfer. Unstrained neutral hydrazines prefer nearly tetrahedral nitrogens and a lone pair–lone pair dihedral angle θ near 90° (see **I**). Unstrained



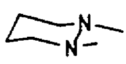
I

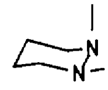

syn


anti

hydrazine radical cations prefer nearly planar nitrogens (lone pair hybridization near pure p), have a strong preference for coplanar lone pair axes ($\theta = 180$ or 0°), and have an N—N bond length about 10% shorter than neutral hydrazines. A modest amount of bending at nitrogen in hydrazine cation radicals is extremely easy, and there are two types of conformations which keep the lone pair axes in the preferred coplanar arrangement, *syn* and *anti* bent ones. In bent species, the stabilized π-rich lone pair combination orbitals mix with the nitrogen σ bond orbitals, and as shown by spectroscopic results,[2] this mixing proves to be substantially greater for *syn* than for *anti* bent structures.

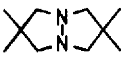
An additional point of interest is that the pyramidality at nitrogen (and hence the lone pair hybridization) in the neutral form proves to be rather sensitive to θ. The effect on lone pair energy is rather large. The average lone pair energy of the diequatorial alkyl group form of dimethylhexahydropyridazine, **ee**, is 14 kcal mol^{-1} stabilized relative to that of the axial–equatorial form **ea** in the gas phase.[3] The ionization

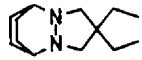

ee


ea

potentials of these conformations are, however, the same because the lone pair–lone pair splitting is much higher for the θ *ca* 180° **ee** than for the θ *ca* 60° **ea**. Low temperature cyclic voltammetry (CV) experiments have demonstrated that **ea** has a much smaller heterogeneous electron transfer rate constant than does **ee**, which we have attributed to their difference in θ values.[4]

Testing the effect of hydrazine geometry on the electron transfer rate requires study of hydrazines having a wide range of θ values. Acyclic hydrazines have θ near 90°, hexahydropyridazines exist as mixtures of 60° and 180° conformations, the ratio depending upon substituents, and bicyclic hydrazines which have one CNNC dihedral angle held near 0° have θ near 120°. Because of the inherent preference for perpendicular lone pairs, $\theta = 0°$ hydrazines will only result when structural features force the CNNC angles on both sides to be near 0°. Prior to this work, only four tetraalkylhydrazines for which θ near 0° conformations were occupied were known, **1–4**, except for diaziridine derivatives. The gem-dialkyl pyrazolidine rings of **1–3**


1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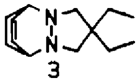
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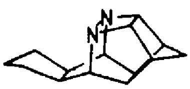
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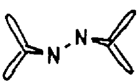
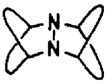
apparently force envelope conformations with the gem-dialkyl carbon out of the plane of the other four atoms, as photoelectron spectroscopy studies indicate a 0° θ value for these compounds. Compound **2** is the most easily oxidized hydrazine known at $E^{\circ\prime} = -0.20$ V (vs SCE in acetonitrile containing 0.1 M tetra-n-butylammonium perchlorate, used throughout this work), presumably because of steric compression in the neutral form which is relieved when the nitrogens flatten upon electron removal. The polycyclic caged hydrazine **4**, prepared by methods developed by Bernig and Hünig,[5] is the most thermodynamically difficult tetraalkylhydrazine to oxidize ($E^{\circ\prime} = 0.81$ V[6]) yet reported, presumably because the geometry about the nitrogens cannot relax much upon electron removal. Although diaziridine derivatives have very high fractions of s hybridization in their lone pairs because of their small CNC angles and are doubtless more difficult to oxidize, they show irreversible electrochemistry, so the thermodynamics of their electron transfers have not been accurately measured.

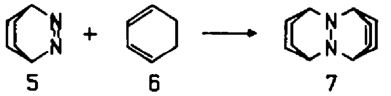
Establishing the detailed geometry of the cation radical requires its isolation and X-ray crystallographic structure determination. Tetraalkylhydrazine cation radicals have only proven isolable when their structures hold the C_α—H bonds perpendicular to their p-rich lone pair orbitals, a structural features we have called "Bredt's rule protection".[7] This has been accomplished with *bis*-N,N-bicycloalkyl structures **II**, which are easily made by coupling the bicyclic N-chloroamine monomers with alkyllithiums.[1] These tetra-β-branched hydrazines have proven to exist in $\theta = 180°$ conformations in the neutral form, and the bicyclic rings usually force the CNC angles to be smaller than in unstrained hydrazines and cause the radical cations to be *anti* bent. We felt it would be important to study the *bis*-N,N'-bicyclic hydrazines exemplified by **III**. Since they are Bredt's rule protected like **II**, one would expect them also to have isolably stable radical cations. The structural constraints of **III** are substantially different than those of **II**. For **III**, the CNC angles are forced to be unusually large, and both CNNC dihedral angles are held near 0°, which ought to lead to 0° θ values in the neutral compound. The unusually large non-bonded interactions in the neutral compound might lead to nitrogen atoms which are flatter than usual, causing $E^{\circ\prime}$ values to be unusually low and geometry changes between the neutral and radical cationic forms to be smaller than usual, giving faster kinetics for electron transfer. The availability of hydrazines **III** with various ring sizes would allow examination of a series of θ near 0° compounds with varying amounts of pyramidality at nitrogen and non-bonded interactions, and for study of electron transfer equilibria and kinetics, as well as π–σ mixing in their radical cations. This work describes a method for the synthesis of hydrazines of type **III** and the electron transfer thermodynamics of several examples.[8]


II

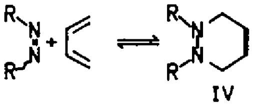

III

Results

Preparation of **III**. Synthesis of **III** by alkylation methods did not seem attractive because elimination would be a problem. Diels–Alder addition of an azo compound to a cyclic diene, shown for the case of 2,3-diazabicyclo[2.2.2]oct-2-ene (**5**) and cyclohexadiene (**6**) to give adduct **7** (Eq. 2) is obviously an attractive route to an example of **III**, but a survey of the literature did not reveal successful addition of any azoalkane to any diene (Eq. 3). The *retro* reaction, thermal cleavage of tetrahydropyridazines **IV** is a well-known process, which has been studied for several R = methyl cases in bicyclic systems, showing unusual stereochemistry.[9] Although only the *trans* methyl isomer **8sa** is observed spectroscopically for 2,3-dimethyl-2,3-diazabicyclo[2.2.2]oct-5-ene (**8**), its thermal cleavage gives a *z/e* ratio of the azomethane formed of 5.6.[10] This indicates that the activation energy for retro-Diels–Alder cleavage of the undetected **8ss** isomers (and/or its **8aa** isomer) is smaller than that for the **8sa** isomer by more than the ground state energy difference between **8sa** and **8ss**, a result which is the opposite of that we would expect based on steric interactions. In agreement with this result, the tricyclic analogue of **8** which is most stable in the *cis* fused geometry, **3**, has a half-life at 100° of about 16 min, while the decomposition of **8** is considerably slower, and was studied at 250°.[10] The low thermal stability of **3** makes it clear that the addition reaction of Eq. (2) would have to be achieved at a low temperature to have any hope of isolating adduct **7**.



(2)



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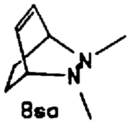
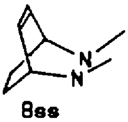
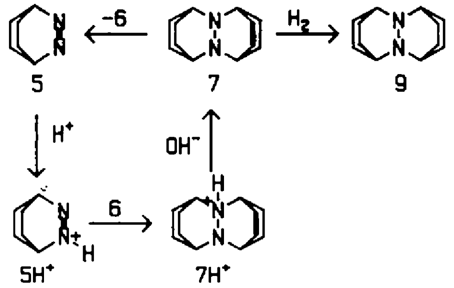


8sa



8ss

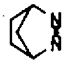
In attempts to use acid to catalyze the addition of Eq. (2) we discovered that a stoichiometric amount of HBF_4 makes the addition proceed efficiently, but that excess acid polymerizes the cyclohexadiene more rapidly than it adds to the azo compounds (Scheme 1). A convenient way to run the reaction proved to be to carefully pump excess reagent off the solid $\mathbf{5}H^+BF_4^-$ produced by treatment of **5** with fluoroboric acid etherate and to conduct the reaction with cyclohexadiene in acetonitrile at 50°. Heyman and Snyder[11] were the first to report isolation of protonated bicyclic azo compounds, as the perchlorate salts. Although **7** is isolable at room temperature, it slowly cleaves. Compound **7** is efficiently reduced to **9** by Pd/$BaCO_3$ in ethyl acetate with added potassium carbonate, but more than 1 mol of hydrogen was absorbed with several other catalyst–solvent combinations. All four steps of



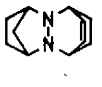
Scheme 1.

Scheme 1 are efficient, and **9** was obtained in 93% overall yield from **5**.

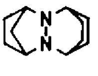
2,3-Diazabicyclo[2.2.1]hept-2-ene **10** was also used for the reaction, allowing preparation of **11** and **12** from cyclohexadiene, and **13** and **14** from 1,3-cycloheptadiene.



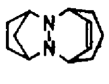
10



11



12



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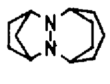
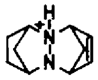
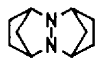


14



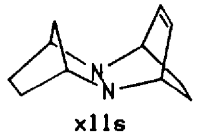
15H$^+$



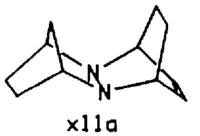
16

As might be expected, addition to **10H$^+$** is more rapid than to **5H$^+$**, and cyclohexadiene adds more rapidly than does cycloheptadiene. We were concerned that the greater sensitivity to acid of cyclopentadiene than the larger cyclic dienes might make **10H$^+$** polymerize cyclopentadiene faster than it adds, but we were able to successfully isolate **15H$^+$** and, after diimide reduction, to obtain the saturated III adduct **16**. Deprotonation of **15H$^+$** at room temperature just gave **10** and cyclopentadiene, cleavage of **15** being complete before a ^{1}H-NMR spectrum could be recorded.

The dissymmetry of **10** with respect to its CNNC plane makes two isomeric adducts available with cyclic dienes, exemplified by the cyclohexadiene adducts **x11s** and **x11a** shown below. We employ x for *exo* and n for *endo* with respect to the [221] system derived from the azo compound, and s for *syn* and a for *anti* with respect to the olefin group remaining from the diene after Diels–Alder addition. The *endo* conformations are related to those shown by double nitrogen inversion but are more sterically crowded, and would isomerize to the above conformations even if they were formed faster. To get a feeling for the relative energies of these conformations, we have carried out Allinger MM2 calculations[12] on the related hydrocarbons A (Table 1). No force is yet available for any molecule with bonded heteroatoms, and although the hydrocarbons A will obviously have slightly different preferred bond lengths and angles at the central carbons than the nitrogens of hydrazines **11**, we suggest that because the principal steric differences are similar for isomers of A and **11**, the energy ordering of the conformations ought to be the same. Table 1 gives the steric energies, the average of the three valence bond angles at C_2 and at C_7 (α_{av}), and the dihedral angle between the rings fused at positions 2 and 7 (ϕ_{av}). As expected, conformation **xAs** is calculated to be the most stable conformation. Having the diene add *endo* to the bicycloheptene system (**nAs**) or the bicycloheptene system *anti* to the double bond of the bicyclooctene system (**xAa**), introduces more steric energy and causes flattening at C_2, C_7, as indicated by the increase in α_{av} and ϕ_{av}.

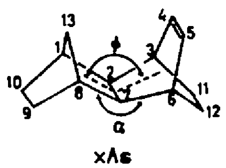


x11s



x11a

Table 1. Results of MM2 calculations on *cis*-fused tetracyclo[6.2.1.1^{3,6}.0^{2,7}]tridec-4-enes, A



xAs

Compound	Steric energy (kcal mol^{-1})	α_{av} (°)	ϕ_{av} (°)
xAs	42.3	109.7	125.5
xAa	45.0	110.6	128.1
nAs	44.8	111.3	130.2
nAa	51.5	112.6	134.8

Only one isomer of **11** was detected by NMR, and it shows a large separation between the signals for the two protons attached to C_{13}, which appear at 0.64 (br. d., J = 10 Hz) and 2.42 δ (br. d., J = 10 Hz). In the hydrogenated compound **12**, these protons come at 1.25 and about 2.10 δ (overlapped by protons at C_9, C_{10}). We suggest that these chemical shifts for **11** may only be rationalized for the **x11s** conformation, where the C_{13} methylene group is forced into the shielding region of the $C_4{=}C_5$ bond. Similarly, only one isomer was observed for **13** and **15H$^+$**, and the diazabicycloheptane one carbon bridge must be *syn* to the vinyl group of these compounds also, from the chemical shifts of the protons (Experimental). All three cases, then, give the stereochemistry of approach to the diene predicted by the Alder *endo* rule if attack is from the less hindered *exo* face of the azo compound. Because MM2 calculations on the related hydrocarbons give the result that this adduct is also the thermodynamically most stable one, this may not be a kinetic result. Nevertheless, only the products having the two carbon bridge formed from the diene *syn* to the one carbon bridge resulting from the azo compound were formed in a detectable amount.

Results and discussion

Proton driven Diels–Alder reactions. In previously unpublished work, Hollinsed[10] studied the cleavage of **3** to **6** and azo compound 4,4-diethylpyrazoline in DMSO-d_6, finding a half-life at 69° of 12.8 h, corresponding to $\Delta G^\ddagger$ (69°) of 27.7 kcal mol^{-1}. Studies over a temperature range of 69–99° gave $\Delta H^\ddagger$ = 31.2±1.0 kcal mol^{-1}, $\Delta S^\ddagger$ = 10.4±2.7 cal deg.$^{-1}$ mol^{-1}. The cyclohexadiene adducts of diazabicyclooctene **5** and diazabicycloheptene **10** are significantly less thermally stable than this. Only rough kinetics at one temperature have been determined by ^{1}H-NMR for **7** and **11**, following their decomposition in CDCl$_3$. Half-lives at 50° of 2.1 h for **7** (corresponding to $\Delta G^\ddagger$ *ca* 25.1 kcal mol^{-1}) and 5.5 h for **11** ($\Delta G^\ddagger$ *ca* 25.5 kcal mol^{-1}) were observed. Engel[13] has measured the strain energy of **10** to be 5.3 kcal mol^{-1} greater for **10** than that of 1,4-dimethyl-**5**. For comparison, MM2 calculations[12] on the hydrocarbon analogues (N replaced by CH) give a 3.2 kcal mol^{-1} greater steric energy for the analogue of **11** than for that of **7**, but give a 4.2 kcal mol^{-1} lower steric energy release upon cleavage for the hydrocarbon analogue of **11** than for that of **7**, so a prediction of which transition state would lie lower in energy for the hydrocarbons is not clear. Similar rates for decomposition of **11** and **7** seem plausible, but we certainly would not have been able to confidently predict which should have been the stabler towards *retro*-Diels–Alder reaction. As stated above, the diazanorbornene–cyclopentadiene adduct **15** is much less stable than either **7** or **11**, and cleaves rapidly at room temperature. The hydrocarbon analogue of **15** is calculated to have a 9.8 kcal mol^{-1} higher steric energy than that of **11**, and to release 8.4 kcal mol^{-1} more strain upon *retro*-Diels–Alder cleavage, so the instability of **15** is expected.

In no case was any adduct observed at equilibrium, indicating that the Diels–Alder addition reactions giving **III** are endothermic. Diels–Alder reactions are usually reliably exothermic, because two π bonds are converted to two σ bonds during the reaction, which is usually exothermic enough to over-ride other factors. Not only does Eq. (2) introduce an unusual amount of strain for a Diels–Alder reaction (all four carbons α to the N—N bond of the product are branched), but an unusually weak σ bond is produced, the N—N bond in its least stable $\theta = 0°$ configuration. The acid of Scheme 1 cannot simply be catalyzing addition of the azo compound to the diene; a catalyst does not make an endothermic reaction occur. The acid provides a favorable driving force for the addition reaction, as shown in the schematic free energy diagram of Fig. 1. At the top is shown the endothermic reaction of **5** and **6** (the energy of the pair is shown as a) to give **7** (the energy shown as b). We wrote a free proton on each side of the top equation, which does not change the relative energy of a or b. The azo compound is a weak base, and will protonate, giving **5H**$^+$ and **6**, with an energy shown as c. The a–c energy gap represents the "strength" of the N—H bond of **5H**$^+$. Hydrazines are much stronger bases than are azo compounds, and the energy gap from b to **7H**$^+$ (which appears at energy d) will be greater than the a–c gap. The bottom equation is clearly exothermic, as the addition reaction goes in high yield.

Table 2. Aqueous pK_a values for **III** derivatives and bicyclic azo compounds

Compound	pK_a
7H$^+$	9.73 (4)
9H$^+$	10.37 (2)
11H$^+$	9.05 (1)
12H$^+$	10.02 (2)
5H$^+$	0.4
10H$^+$	−1.4

The question of how much driving force is generated by the acid is obviously a significant one. A factor of ten in an equilibrium constant represents a $\Delta G°$ increment of $-RT \ln 10$, or 1.36 kcal mol^{-1} at room temperature, so the bottom reaction is 1.36 ΔpK_a kcal mol^{-1} more exothermic than the top one, where ΔpK_a = pK_a (protonated hydrazine) $-$pK_a (protonated azo compound). We report room temperature pK_a values in water for some of the molecules of interest in Table 2. The hydrazine pK_a values were determined by titration of a 5 mM solution of the base with 0.01 M HClO$_4$ solution, measuring the pH with a glass electrode. These protonated **III** derivatives all show pK_a values above 9, so they are significantly more basic than tetramethylhydrazine (pK_a of Me$_4$N$_2$H$^+$ is 6×10^{14}). The interplay between electronic and steric effects on hydrazine pK_a values is a complicated topic,

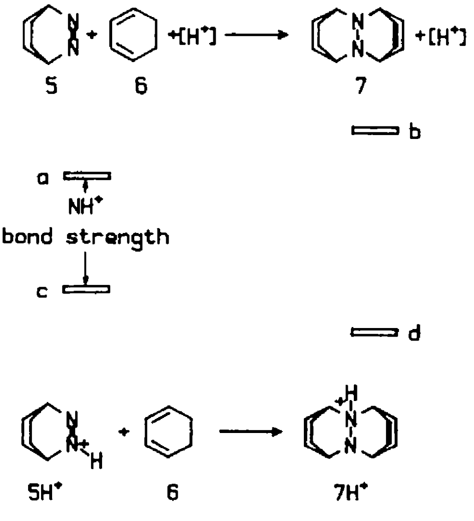


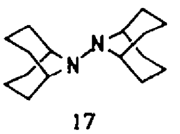
Fig. 1. Energy diagram for Diels–Alder addition of cyclohexadiene to unprotonated and protonated azo compounds.

which will not be discussed in detail here, but since it is clear that more easily oxidized hydrazines are more basic,[15] it is not surprising that **9** is the most basic hydrazine yet studied. The azo compounds were not basic enough to study by direct aqueous titration, and we used the Bunnett and Olsen[16] approach of measuring shifts in ^{1}H-NMR for solutions in aqueous sulfuric acid. The data from Table 2 gives increments in driving force of 9.3 pK_a units (12.6 kcal mol^{-1}) for the addition giving **7** and 10.4 pK_a units (14.1 kcal mol^{-1}) for that giving **11**. Protonation of azo compounds clearly provides a powerful thermodynamic driving force for Diels–Alder reactions, and we suggest that the reactions discussed here may be usefully described as being "proton driven". There seems to be no reason to believe that these reactions have concerted [4+2] cycloaddition mechanisms. Such reactions are extremely sensitive to steric hindrance, and these cases may well go through cationic intermediates.

The above thermodynamic considerations are independent of mechanism, and one could imagine a tiny equilibrium concentration of adduct (such as **7** in Scheme 1) being protonated by acid to remove **7**, driving the unfavorable **5**+**6** equilibrium by removal of product. It seemed unlikely that this would be the case, because with HBF_4 as the acid, extremely little unprotonated **5** would be present in the solution, and there seems little doubt that **5H**$^+$ would add faster to a diene than would unprotonated **5**. The huge pK_a difference between **5** and **7** makes this idea that one is merely trapping a small equilibrium amount of adduct easy to test. In practice, we were unable to observe any adduct formation upon adding acetic acid to a mixture of either **5** and cyclohexadiene or **10** and cyclopentadiene, even after heating for long periods of time. The use of a strong enough acid to protonate the azo compound seems to be experimentally necessary to get the addition reaction to proceed at a useful rate.

Results and discussion

Isolation of a tetraalkylhydrazine dication. Although the kinetically protected *bis*-N,N-bicyclic hydrazines (type II) 9,9 - bi - 9 - azabicyclo[3.3.1]nonane,[7] **17**, and 8,8′ - bi - 8 - azabicyclo[3.2.1]octane,[17] **18**, exhibit



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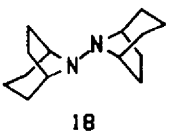

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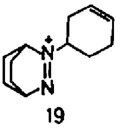
reversible second oxidation waves by CV, showing that their dications last seconds in acetonitrile solution, they do not appear to be very much longer-lived than this. Two-electron oxidation with $NO^+PF_6^-$ ($E^{\circ\prime}$ (NO, NO$^+$) is 1.27 V under our conditions) is only slightly exothermic for these compounds, and NMR studies showed that the dications were formed more slowly than they decomposed when two-electron oxidation was attempted. The low $E_2^{\circ\prime}$ value for **9** of 0.86 V makes formation of 9^{2+} using NO$^+$ significantly exothermic, and gas is vigorously evolved when **9** is mixed with $NO^+PF_6^-$. ^{1}H-NMR studies showed that 9^{2+} formation is efficient, and it proved isolable in 81% yield by vapor diffusion crystallization from the acetonitrile solution with ether. The NMR chemical shifts of 9^{2+} show large downfield shifts from those of **9**; in the ^{1}H-NMR, the bridgehead hydrogens are shifted from 2.71 to 6.23 δ, and the methylene hydrogens from 2.27 and 1.64 to 2.73 and 2.11 δ, while the bridgehead carbons move from 52.8 to 81.3 δ and the methylene carbons from 28.1 to 30.3 δ. The most interesting spectral properties of 9^{2+} salts are their UV spectra. We observe in acetonitrile λ_m, nm (ε) 227 (8400), 317 (2600) for $9^{2+}(PF_4^-)_2$ and 224 (5200), 314 (1500) for $9^{2+}(BF_4^-)_2$. The small shifts upon changing counterion imply that charge transfer between the ions is not important in these transitions. The long wavelength band is not caused by π,π^* absorption, which will be at longer wavelength for the radical cation 9^+ than for 9^{2+}. The radical cation has one electron in the π^* orbital, which ought to lower the π–π^* energy gap substantially relative to the filled π–empty π^* gap of 9^{2+}, yet the long wavelength maxima observed for the two 9^{2+} salts are 50 and 52 nm red shifted from the π–π^* maxima of those salts of 9^+. The unusually large nitrogen charge density of 9^{2+} should strongly stabilize both π and π^* relative to those of the radical cation which ought to make the σ–π^* gap of 9^{2+} unusually small. We suggest that the band near 315 nm should be assigned to such a transition. MNDO calculations on 9^{2+} give the π orbital lower in energy than the σ orbitals, a very unusual result which is in keeping with the unusual charge density stabilization of the π orbital, but we obviously do not know how accurate MNDO calculations on such a species are. A shoulder at 260 nm in the UV spectrum of 17^+ has been assigned to a σ–π^* absorption band,[18] but the expected substantial differences in both σ and π orbital energies of 17^+ and 9^{2+} do not allow a reasonable comparison of the observed UV maxima.

The solid $9^{2+}(PF_6^-)_2$ obtained from acetonitrile solution is an acetonitrile solvate with beautifully developed crystal faces. Although ^{1}H-NMR measurements on freshly prepared material indicate two acetonitrile molecules per 9^{2+} unit, solvent is rapidly lost upon exposure to air, and we have observed ratios as low as 0.5 on old material. The combustion analysis was consistent with a ratio of 1.8. The crystals rapidly become opaque upon removal from acetonitrile, and despite many tries, we have been unable to mount the crystals for X-ray crystallography, even in capillary tubes containing acetonitrile, without losing diffraction, presumably caused by solvent loss, nor have we yet been able to grow X-ray quality crystals which do not contain solvent.

Although 9^{2+} is a powerful oxidant, its NMR spectrum persists for hours in water, so it is surprisingly unreactive to nucleophilic addition. Attempted reactions on 9^{2+} under several conditions gave a similar product, which shows three multiplets between 5 and 6 δ in its ^{1}H-NMR spectrum. We believe, but have not proven, that this product comes from N—C bond cleavage and deprotonation, giving **19**.



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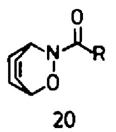

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NO$^+$ oxidation of **7** does not give 7^{2+}, but causes decomposition of the tetracyclic system. This is not surprising, because 7^{2+} has allylic C—N bonds. We

Table 3. Electrochemical data for bis-N,N'-bicyclic hydrazines[a]

Compound	$E_1^{\circ\prime}[\Delta E_p]$ (V)	$E_2^{\circ\prime}[\Delta E_p]$ (V)
7	−0.25 [0.07]	0.95 [0.08]
9	−0.53 [0.07]	0.86 [0.07]
11	+0.06 [0.08]	0.95 [0.09]
12	−0.26 [0.07]	0.92 [0.08]
13	−0.04 [0.07]	1.04 [0.08]
14	−0.22 [0.10]	1.01 [0.09]
16	+0.01 [0.10]	1.12 [0.17]

[a] Room temperature, 1–2 mM hydrazine in acetonitrile containing 0.1 M tetrabutylammonium perchlorate, 200 mV s^{-1} scan rate, at a gold electrode, vs SCE.

already know that the cation radicals from 3-acyl-2-oxa-3-azabicyclo[2.2.2]oct-5-enes **20** are short-lived at room temperature, in contrast to their 5,6-saturated analogues,[19] and the same trend occurs for bicyclic peroxide radical cations,[20] where the unsaturated compounds are short-lived even at low temperature, although their saturated analogues are long-lived even at room temperature. We suggest that $\mathbf{7}^{2+}$ cleaves an allylic N—C bond, producing principally a diene analogue of **19**, which is consistent with the NMR spectrum of the crude decomposition product.

Results and discussion

Thermodynamics for electron loss. The thermodynamically significant formal potentials for oxidation of bis-N,N'-bicyclic hydrazines are summarized in Table 3. Compound **9** is noteworthy as the most easily oxidized tetraalkylhydrazine yet reported. It is 19.8 kcal mol^{-1} easier to remove an electron from **9** than it is from tetramethylhydrazine, and not surprisingly, **9** is rather air sensitive. Samples exposed to air contain enough radical cation to give a strong ESR spectrum. The reason for the easy oxidation of **9** is clearly the fact that neutral **9** is quite strained. The *syn* dimethylene bridges of its bicyclo[2.2.2]octyl groups are pushed into each other unless the nitrogens are unusually flattened. Sterically induced flattening at nitrogen is especially costly in energy for **9** because its bicycloalkyl groups force both internal CNNC angles to be near 0°, so θ must be near 0°. When the nitrogen lone pairs of a hydrazine are forced to lie near coplanarity, the nitrogens prefer to increase their lone pair s hybridization to lengthen the N—N bond and decrease lone pair–lone pair overlap.[1] Non-bonded steric interaction should be reduced in $\mathbf{9}^{+}$, because hydrazine radical cations prefer much flatter nitrogens than do neutral hydrazines. The range in ease of oxidation of the *bis*-N,N'-bicyclic hydrazines of Table 3 is quite large, corresponding to a 12.5 kcal mol^{-1} more difficult electron loss from **16** than from **9**. Changing one bridge on each side of the molecule from two carbons to one will clearly decrease the size of non-bonded interactions in the neutral compound, and also ought to make a planar radical cation more strained, so it is not surprising that $E^{\circ\prime}$ is more positive for **16** than for **9**. We have explored the question of whether the $E_1^{\circ\prime}$ values of Table 3 may be quantitatively understood in terms of steric interactions between the rings by using MM2 calculations.[12] No force field is available for hydrazines, but the important non-bonded steric interaction differences between different compounds in Table 3 ought to be similar for the hydrazines and their hydrocarbon analogues with N replaced by CH, despite the substantially more difficult flattening at the central bridgehead positions in the hydrocarbons and the minor differences in preferred bond lengths. One would certainly not expect the steric energies of the hydrocarbons to reflect those of the hydrazines because of these differences, but the trends in change of geometry as the steric interactions are changed ought to be similar, and we have compared first $E^{\circ\prime}$ with the geometric parameters reflecting sterically induced geometry change at the central bridgehead carbons, α_{av} and ϕ_{av}. Figure 2 demonstrates that there is a surprisingly good correlation between the hydrazine $E^{\circ\prime}$ and the calculated hydrocarbon analogue α_{av} for 0° hydrazines. The line shown is based on the saturated *bis*-N,N'-bicyclic compounds **9**, **12**, **14**, and **16**, as well as the monobicyclic **2** and bis-monocyclic **1**. The only compound to deviate more than 0.04 V in $E^{\circ\prime}$ from the line ($r = 0.95$, average deviation 0.04 V) is **12**; its deviation is −0.12 V. A similar plot of $E^{\circ\prime}$ vs ϕ_{av} shows more scatter ($r = 0.82$, average deviation 0.08), and places **12** close to the line while moving **16** substantially off the line (deviation +0.21 V). The unsaturated hydrazines **7**, **11**, and **13** are each substantially harder to oxidize than their saturated analogues, and the fact that each is also less strained is clearly important. For less constrained examples, a tetrahydropyridazine has been found to be 0.10 V harder to oxidize than its hexahydropyridazine analogue,[16] presumably because of the inductive difference between the vinyl and saturated carbon atoms. When 0.10 V is subtracted from the observed $E^{\circ\prime}$ for **7**, **11**, and **13**, to allow for this inductive difference, these compounds also fit the line well in Fig. 2; they are shown as open squares. Although the correlation of Fig. 2 works surprisingly well for these type III hydrazines, hydrazines with dihedral angles substantially different from 0° are far harder to oxidize than the line in Fig. 2 predicts, whether or not these compounds contain bicycloalkyl part-structures; the compound coming closest to the line we have found yet is 1,5-diazabicyclo[3.3.0]octane, the dimethylated analogue of **1**, which falls +0.13 V from the line. Its θ value is estimated at 30° from its photoelectron spectrum,[17] so it also has significantly interacting *syn* lone pairs, although they probably have a larger dihedral angle than all of the compounds of Table 3. We suggest that the correlation of Fig. 2 supports the idea that steric differences are the major reason for the wide range in $E^{\circ\prime}$ values of Table 3, and expect it to be useful in predicting oxidation potentials for other 0° hydrazines. We do not of course, expect that the α_{av}

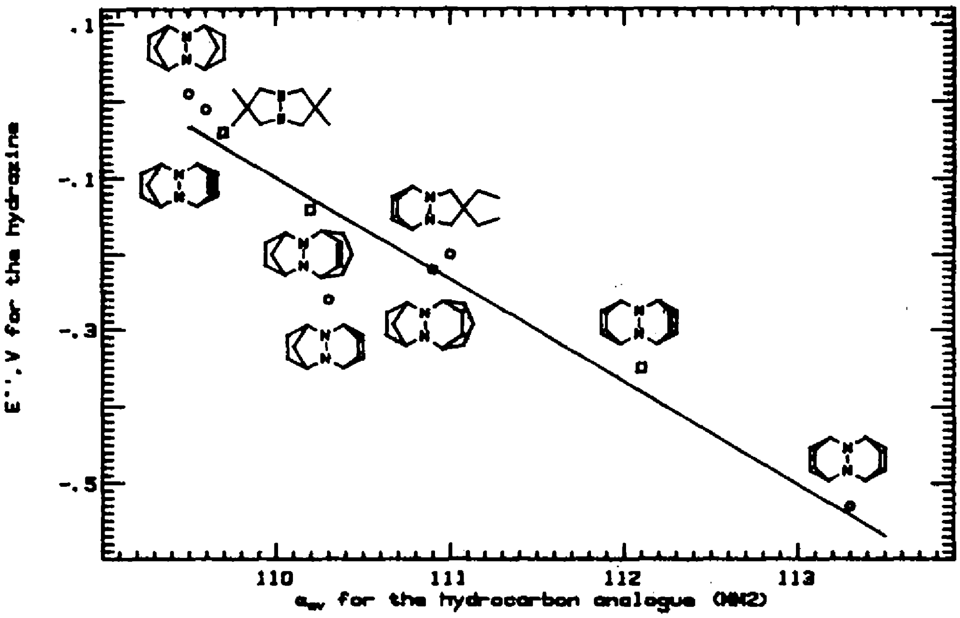

Fig. 2. Plot of formal oxidation potential for $\theta = 0°$ hydrazines vs the average of the bond angles to carbon of the carbons at the zero atom bridge in their hydrocarbon analogues (N replaced by CH), as given by MM2 calculations.

values calculated for the hydrocarbon analogues will necessarily be close to those of the hydrazines, nor that the changes in $E^{\circ\prime}$ observed reflect only strain in the neutral form.

The *bis*-N,N'-bicyclic hydrazines of Table 3 are all kinetically protected against deprotonation of their oxidized forms, and it is not surprising that they all show reversible second electron loss by CV. $E_2^{\circ\prime}$ for **9** is the smallest yet measured, at 0.86 V, but $\Delta E° = E_2^{\circ\prime} - E_1^{\circ\prime}$ is the largest, at 1.39 V, corresponding to an endothermicity for electron transfer disproportionation ($2[9^+] \rightarrow 9^{2+} + 9°$) of 32 kcal mol^{-1}. The decrease in non-bonded interaction which accompanies flattening upon loss of the first electron is substantial, but further flattening upon loss of the second electron probably costs very little energy, and also releases little or no additional steric strain. Solvation effects might also be involved in making $\Delta E°$ unusually large for **9**. We have previously noted that $E_2^{\circ\prime}$ for 8,8'-bi-8-azabicyclo[3.2.1]octane is 1.14 V for the *anti* isomer, but substantially lower at 1.01 V for the *syn* isomer, although both steric and electronic interactions would lead one to expect that the *anti* isomer would be, if anything, slightly easier to oxidize than the *syn* isomer.[17b] We suggested that since the difference observed cannot be rationalized on the basis of the organic cations alone, it was most likely that solvent and/or counterion approach to the nitrogens was involved in causing the observed result. The nitrogens of all these examples of **III** are certainly unusually well protected by their alkyl groups from close approach of solvent and counterion.

We now consider more quantitative comparisons of the difference in ease of oxidation between saturated (S) and unsaturated (U) examples of these type **III** hydrazines. Steric interaction between the *syn* bridges is decreased when the nitrogens flatten out upon electron removal. If this flattening decreased the steric interaction between the *syn* bridges to a negligible value in both the S and U examples, as it would if the nitrogens were flat enough in the cation radicals, the difference in $E_1^{\circ\prime}$ values would allow calculation of the difference in steric strain between the S and U compounds, because $\Delta E_1^{\circ\prime} = E^{\circ\prime}(\mathrm{U}, \mathrm{U}^+) - E^{\circ\prime}(\mathrm{S}, \mathrm{S}^+)$ is equal to an inductive term and a steric term, and the inductive term is known to be about 0.10 V. See Fig. 3 for a graphical depiction of the potentials used here. We therefore expect that when the nitrogens of the cation radicals are flat enough, Eq. (4) will hold:

Steric strain difference,

$$\text{kcal mol}^{-1} = 23.06\,(\Delta E_1^{\circ\prime} - 0.10) \qquad (4)$$

where $\Delta E^{\circ\prime}$, $V = E^{\circ\prime}(\mathrm{U}, \mathrm{U}^+) - E^{\circ\prime}(\mathrm{S}, \mathrm{S}^+)$. For **9** and **7**, Eq. (4) gives a 4.2 kcal mol^{-1} greater strain energy for neutral **9**, the S compound, than for the U compound **7**. A separate estimate of the steric strain difference between **9** and **7** can be made by comparing the difference in the ease of first and second electron loss for

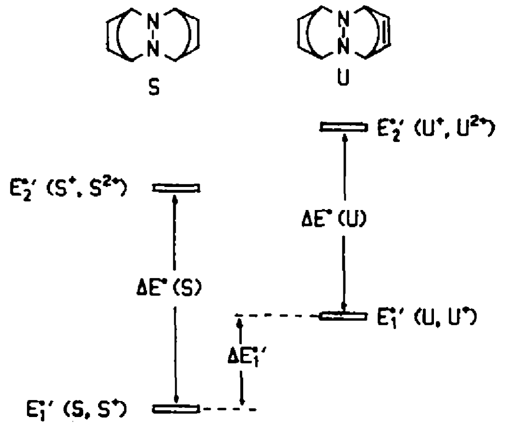

Fig. 3. Energy diagram relating the oxidation potentials of saturated and unsaturated type III hydrazines.

these compounds. If all of the steric strain difference between **9** and **7** is released upon loss of the first electron, none is left to affect the second electron loss, and the inductive effects should cancel because the U and S compounds are considered separately. The unsaturated compound U should have a smaller $E_2^{\circ\prime} - E_1^{\circ\prime}$ value than the saturated compound S by the size of the same steric strain term as in Eq. (4), so we argue that if Eq. (4) is valid, Eq. (5) should also hold:

Steric strain difference,

$$\text{kcal mol}^{-1} = 23.06\,(\Delta\Delta E^\circ), \tag{5}$$

where $\Delta\Delta E^\circ$, $V = \Delta E^\circ(\text{S}) - \Delta E^\circ(\text{U})$. Equation (5) gives 4.4 kcal mol^{-1} greater strain in **9** than in **7**, within experimental error (about 0.2_3 kcal mol^{-1}, 0.01 V) of that given by Eq. (4). Getting the same numbers from Eqs (4) and (5) suggests to us that our assumption that the nitrogen of both cation radicals are flat enough so there is little steric interaction between the *syn* bridges in the cation radicals is at least approximately correct. Similarly, comparing **14** with its unsaturated analogue **13** gives a 1.8 kcal mol^{-1} greater steric strain in **14** using Eq. (4) and a 1.6 kcal mol^{-1} difference using Eq. (5), again within our experimental error of being the same.

Equations (4) and (5) obviously will not hold if there still is significant steric interaction between the *syn* bridges in either radical cation, or if the strain energy caused by angle strain at the nitrogen atoms differs significantly for the S and U compounds being compared. This appears to happen for **12** and **11**, where the smaller bicyclic rings presumably force α_{av} to be smaller. Here Eq. (4) gives 5.1 kcal mol^{-1} (0.22 V) and Eq. (5) gives 6.7 kcal mol^{-1} (0.29 V), values which differ significantly compared to experimental error. It is certainly not obvious that either value is close to the steric energy difference between these two compounds, which we would have guessed would be smaller than for **9** vs **7**. This is the result obtained for the hydrocarbon analogues by MM2 calculations, although we note that **12** deviates badly in the plot of Fig. 2, the observed $E^{\circ\prime}$ being significantly more negative than the MM2 calculations on the hydrocarbon analogue predicted. We unfortunately cannot examine what happens in the next lowest homologous pair, because **15** proved to be too unstable to isolate.

CONCLUSIONS

The "proton-driven" Diels–Alder reaction of protonated azo compounds with cyclic dienes makes efficient preparation of *bis*-N,N′-bicyclic hydrazines of type **III** possible. The nitrogens of **9** are forced to be unusually flattened, resulting in **9** being the most easily oxidized hydrazine yet prepared, and it is also the first hydrazine to give an isolable dication. Other examples of **III** prepared here have significantly varying amounts of non-bonded interaction and degrees of planarity in both the neutral and radical cation oxidation states, but all probably have lone pair–lone pair dihedral angles θ rather near 0°. We expect this series of compounds to prove significant for probing structural effects on the size of geometry change between oxidation states of organic compounds, relating the size of the geometry change to the kinetics for electron transfer and for establishing the relationship between the amount of pyramidality at nitrogen and spectral properties.

EXPERIMENTAL

Preparations of **7H**$^+$, **7**, **9**, **9**$^+$NO$_3^-$, and **9**$^{2+}$(PF$_6^-$)$_2$ have appeared in the supplementary material of Ref. 8.

2,3 - *Diazabicyclo*[2.2.1]*hept - 2 - ene tetrafluoroborate* (**10H**$^+$). A soln of 1.51 g (0.0157 mol) of **10** in 25 ml of anhyd ether was cooled to 0° and tetrafluoroboric acid diethylether complex (1.91 ml) was added slowly to the stirring soln via a dry syringe. **10H**$^+$ precipitates immediately. The ether was evaporated and 25 ml was again added. After the second evaporation, the solid was evacuated (0.03 Torr) for 2 h, and stored under N_2 at 0° for later use.

syn - 2,7 - *Diazatetracyclo*[6.2.2.1^{3,6}.0^{2,7}]*tridec* - 9 - *ene* (**11**). One equivalent of $HBF_4 \cdot Et_2O$ (3.01 ml) was added to a stirred soln of 2.0 g **10** (21 mmol) in 20 ml acetonitrile, the mixture was cooled to 0°, and 1 equiv of cyclohexadiene was added (2 ml) to yield a clear, slightly yellow soln. After 16 h at 0°, ^{1}H-NMR showed that the reaction had gone to completion. The crude product was precipitated by adding dry ether, and isolated by filtration. Washing with Et_2O and drying gave 4.2 g of **11H**$^+$ (75% yield). To a stirred mixture of 10 g powdered NaOH in 60 ml dry ether was added 2 g of this material. After stirring under N_2 for 2 h, the solid was removed by filtration, and the ether evaporated to yield 1.24 g of crude **11**. Recrystallization from hexane at −78° gave 0.96 g of **11** (72% yield from **11H**$^+$, 54% yield overall), m.p. 85–86°; ^{1}H-NMR ($CDCl_3$): δ 6.33 (t[J = 4.4], $H_{9,10}$), 3.60 (br.s, $H_{1,8}$), 3.45 (br.s, $H_{3,6}$), 2.42 (br.d [J = 10.4], H_{13a}), 2.0 (br.d[J = 7.4], $H_{11s,12s}$), 1.26–1.60 (m, $H_{4s,5s}$, $H_{4a,5a}$), 1.12 (br.d[J = 7.4], $H_{11a,12a}$), 0.64 (d[J = 10.4], H_{13s}); ^{13}C-NMR {^{1}H} (acetone-d$_6$): δ 133.9 ($C_{9,10}$), 63.3 ($C_{3,6}$), 54.5 ($C_{1,8}$), 33.5 ($C_{4,5}$), 31.9 (C_{13}), 26.0 ($C_{11,12}$); empirical formula $C_{11}H_{16}N_2$ established by high resolution MS.

2,7 - *Diazatetracyclo*[6.2.2.1^{3,6}.0^{2,7}]*tridecane* (**12**). Pure **11** from above (235 mg, 1.33 mmol) was dissolved in 5 ml EtOAc and added to a H_2 equilibrated mixture of 20 ml EtOAc, 170 mg, 10% Pd on $BaCO_3$ catalyst, and 100 mg K_2CO_3. After absorption of 1 equiv H_2 at atmospheric pressure, H_2 uptake stopped and the soln was filtered through celite. The EtOAc was removed by rotary evaporation to yield 224 mg of **12**, a clean, white solid (yield 95%), m.p. 65–66°; ^{1}H-NMR ($CDCl_3$): δ 3.30 (br s, $H_{3,6}$), 2.72 (br s, $H_{1,8}$), 2.10 (br. d[J = 9.3], H_{13s}, $H_{9s,10s}$), 1.96 (br d[J = 9.3], $H_{11s,12s}$), 1.46–1.70 (m, $H_{9a,10a}$, $H_{4s,5s}$, $H_{4a,5a}$), 1.41 (br. d[J = 9.0], $H_{11a,12a}$), 1.25 (d[J = 10.2], H_{13a}); ^{13}C-NMR {^{1}H} ($CDCl_3$): δ 61.4 ($C_{3,6}$), 49.8 ($C_{1,8}$), 34.2 (C_{13}), 32.3 ($C_{4,5}$), 29.1 ($C_{11,12}$), 22.2 ($C_{9,10}$); empirical formula $C_{11}H_{18}N_2$ established by high resolution MS.

anti - 2,8 - *Diazatetracyclo*[7.2.1.2^{3,7}.0^{2,8}]*tetradec* - 14 - *ene* (**13**). A soln of 0.60 g (33 mmol) of **10H**$^+$ and 0.31 g (33 mmol) cycloheptadiene in 10 ml CH_3CN was stirred and heated at 40° for 16 h, by which time the soln had turned dark yellow. After rotary evaporation of solvent, the solid was washed twice with ether and evacuated, giving 0.276 g (30%) of crude **13H**$^+$. This material was mixed with 20 ml anhyd ether, and 2.5 g crushed NaOH pellets, stirred for 2 h at room temp, and filtered off. Concentration gave crude **13** as a brownish liquid in 31% yield (0.193 g), which was sublimed at 30° to a cold finger cooled with dry ice to give a white solid which melts near room temp. ^{1}H-NMR ($CDCl_3$): δ 6.13 (dd[J = 5.5, 4.4], 2H), 3.30–3.51 (m, 2H), 2.38 (dt[J = 10.8, 2.6], 2H), 1.03–1.92 (m, 10H), 1.78 (d[J = 10.8], 2H); ^{13}C-NMR ($CDCl_3$): δ 130.9 (d), 65.8 (d), 58.1 (d), 32.9 (t, C_{12}), 31.9 (t), 19.1 (t, C_5); empirical formula $C_{12}H_{18}N_2$ was established by high resolution MS.

anti - 2,8 - *Diazatetracyclo*[7.2.1.2^{3,7}.0^{2,8}]*tetradecane* (**14**). Crude **13** (193 mg, 1 mmol) was hydrogenated by the method used for **12**, giving 87 mg crude **14**. Purification by Kugelrohr distillation at 50–70°, 0.03 mm Hg, gave **14** as a white solid, m.p. 28–30°; ^{1}H-NMR ($CDCl_3$): δ 3.35 (br.s, 2H), 2.98 (br.s, 2H), 1.40–2.12 (m, 15H), 1.22 (d[J = 11.1], 1H); ^{13}C-NMR

$\{^1H\}$ (acetone-d_6): δ 64.0 (d), 54.3 (d), 37.7 (t), 34.3 (t, C_{12}), 31.4 (t), 19.6 (t, C_5), 19.1 (t, $C_{13,14}$); empirical formula $C_{12}H_{20}N_2$ was established by high resolution MS.

anti - 2,7 - *Diazatetracyclo*[6.2.1.1^{3,6} . 0^{2,7}]*dodecane* (**16**). 2.78 g **10H**$^+$ (15.7 mmol) in 30 ml CH_3CN were cooled to 0°, and 2 ml (1.55 equivs, 24 mmol) of freshly cracked cyclopentadiene added over a 2 min period, and warmed to room temp for 10 min. The formation of **15H**$^+$ was indicated by ^{1}H-NMR (CD_3CN): δ 6.59 (m, 2H), 4.83 (br.s, 2H), 2.47 (d[J = 11], 1H), 2.00 (d[J = 8], 1H), 1.87–1.58 (m, 5H), 1.24 (d[J = 11], 1H). The mixture was cooled to 0° and transferred via cannula to a 250 ml three neck flask containing 13.5 g $KO_2C—N{=}N—CO_2K$ (4.4 equiv), and 50 ml CH_3CN at 0° and equipped with a reflux condenser. AcOH (10 g, 10.2 equiv) in 30 ml CH_3CN was added via a dropping funnel over a 10 min period. The mixture was kept at 0° and stirred for 3 h, and then stirred overnight at room temp. After gravity filtration, solvents were removed by rotary evaporation followed by evacuation to yield 3.9 g of an orange colored oil. To this residue was added 50 ml Et_2O and 10 g crushed NaOH pellets. After stirring for 3 h, the solid was filtered, and the solvent removed to yield 1.4 g of a slightly yellow liquid, which was Kugelrohr distilled and then sublimed to give 0.96 g (37% yield) of **16** as a clear liquid. ^{1}H-NMR ($CDCl_3$): δ 3.56 (br.s, $H_{3,6}$), 3.40 (br.s, $H_{1,8}$), 2.26 (br.dt [J = 8.2, 2.2], H_{11s}), 1.89 (m, $H_{4n,5n}$), 1.31–1.60 (m, $H_{4x,5x}$, $H_{9x,10x}$, $H_{9n,10n}$, H_{11a}), 1.17 (d[J = 11.1], H_{12a}); ^{13}C-NMR $\{^1H\}$ ($CDCl_3$): δ 61.6 ($C_{1,8}$), 56.5 ($C_{3,6}$), 41.4 (C_{11}), 33.2 (C_{12}), 31.9 ($C_{9,10}$), 25.2 ($C_{4,5}$); empirical formula $C_{12}H_{20}N_2$ was established by high resolution MS.

pK_a *Determination of hydrazines*. The potentiometric experiments were carried out with a Microprocessor pH Millivolt Meter 811 (Orion Research) using a glass Automatic Temperature Compensation probe (Model 917002, Orion Research) as the pH electrode. Before each titration, the pH meter was doubly standardized to achieve a 99 ± 1% slope. Triply distilled water, deaerated with N_2 for 3 h, was used for all solns. Titrations were carried out in a 50 ml 3-neck flask, under N_2, with stirring at 25.0 ± 0.1°. Hydrazines (30 ml of 0.005 M solns) in 0.1 M TEAP were titrated with 0.01 M $HClO_4$. Between each addition of acid, 2–5 min equilibration time was allowed before recording the pH reading. The equivalence point was obtained from a plot of pH vs volume of added base, and the pK_a determined as the pH at half the equivalence point, using a graphics program written by Willi for an IBM PC computer.

pK_a *Determination of azo compounds*. Reagent grade concentrated H_2SO_4 was standardized by titration with standardized NaOH soln. This 95.6 ± 1% H_2SO_4 soln was then diluted by weight with triply distilled H_2O to obtain H_2SO_4 solns of lesser concentrations. Azo compound (0.1 mmol, 0.01 M) and 80 mg (0.05 M) of $Me_3NH^+HSO_4^-$ (as reference) were then dissolved in 10 ml of each concentration of H_2SO_4. Proton FT-NMRs of the solns were obtained on an IBM by presaturating the H^+ peak. Bridgehead chemical shifts were then obtained vs the Me_3N reference peak. Data were analyzed by the method of Bunnett and Olsen.[16] A plot of chemical shift of the bridgehead proton vs %H_2SO_4 shows a clear break. The ionization ratio was calculated as $I = (\Delta\nu_0 - \Delta\nu_x)/(\Delta\nu_x - \Delta\nu_{H^+})$, where $\Delta\nu_0$ is the chemical shift of the neutral azo compound bridgehead hydrogen, $\Delta\nu_{H^+}$ the chemical shift of the fully protonated azo compound, and $\Delta\nu_x$ the observed chemical shift. A plot of $\log(I) + H_0$ vs $H_0 + \log(C_{H^+})$ from the Bunnett–Olsen equation then gives an intercept equal to pK_a, using those points which are on the breaking portion of the titration curve. The slope observed for **5H**$^+$ was -0.542 ($r = 0.995$) and for **10H**$^+$, 0.192 ($r = 0.952$).

Decomposition rates. Samples were run 8–18 mol % in $CDCl_3$ containing t-butylbenzene as an internal standard. Samples were placed in a constant temperature bath (50 ± 1°) for a measured time period, quenched at $-78°$, and the ^{1}H-NMR spectra recorded. The rate of disappearance of the hydrazine was measured by integrating the olefinic protons and comparing this to the integration of the phenyl protons of the internal standard.

Electrochemistry. All electrochemistry was run at ambient temp at approximately 2 mM substrate concentration in CH_3CN (Burdick and Jackson "Distilled in Glass"). Tetra-n-butyl ammonium perchlorate, used as supporting electrolyte, was obtained from Eastman and recrystallized from 1:1 H_2O/EtOH. The gold planar electrode has been described previously.[4] In general, the electrode was polished to a mirror finish and used directly. Cyclic voltammetry was performed in a standard three electrode cell. The counter electrode was a 1 in length of coiled platinum wire, and the reference electrode was a Corning ceramic junction SCE which was isolated from the main compartment by a cracked glass bead. Voltammograms were obtained in a static soln, stirring between scans being accomplished by bubbling N_2 through a syringe needle. The instrument employed consisted of a Princeton Applied Research (PAR) 173 Potentiostat/Galvanometer, a PAR 175 Universal Programmer, and a PAR 179 Digital Coulometer. Scans at a rate below 1 V s^{-1} were recorded on a Houston Instruments "Omnigraphic 2000" *x*–*y* recorder, while those at fast scan rates were photographed from a Tektronix 5000 storage oscilliscope.

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