Conformations of Four-Membered Ring Hydrazines and Hydrazine Radical Cations

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Abstract: Photoelectron spectra of 1,2-dialkyl-1,2-diazetidines show that the 1,2-dimethyl compound (**1**) exists overwhelmingly in the "diequatorial" trans conformation, while a significant amount of the "diaxial" trans conformation is detected for the diisopropyl compound (**2**), and the tricyclic structure holds the diazetidine ring in nearly eclipsed geometry for 3,4-dimethyl-3,4-diazatricyclo[4.2.1.$0^{2,5}$]non-7-ene (**4**) and its saturated analogue (**3**). Although *N*-dimethylaminoazetidine (**5**), *N*-dipropylaminoazetidine (**6**), and biazetidine (**8**) are predominantly in gauche conformations, the anti conformation predominates for *N*-piperidinylazetidine (**7**). The rates of double nitrogen inversion for **3** and **4** are nearly identical and increase slightly with increasing solvent polarity, and $\Delta G^{\ddagger}_{298}$ is about 3.8 kcal/mol lower than for **1**. The ESR splitting constants for the cations from **1, 2,** and **8** are reported, and compared to those for other tetraalkylhydrazine radical cations.

Although many techniques have been used to study the conformations of tetraalkylhydrazines,[2] two of the most useful are NMR and photoelectron (PE) spectroscopy. NMR allows accurate quantitation of the relative amounts of conformations if their interconversion is slow on the NMR time scale, and also determination of the rates for conformational equilibration. NMR does not directly yield information on the dihedral angle between the nitrogen long pairs (θ), but the cis or trans disposition of the *N*-alkyl groups attached to a ring may be established. This allows inferring θ to within several degrees from a knowledge of the CN,NC endocyclic torsional angle allowed by the ring system in bicyclic[2,3] and monocyclic cases.[2,4] The PE technique measures the vertical ionization potentials for the lone pair combination orbitals. Their separation is rather sensitive to θ, experimentally varying from a maximum of 2.3 eV near $\theta = 180$ and 0°[5,6] to a minimum of about 0.5 eV near $\theta = 90°$.[7] The PE time scale is exceedingly short, so even if conformational interconversion is too rapid to be "frozen out" by NMR spectroscopy, the PE spectrum observed is the superposition of those for the conformations present. Although the relative amounts of different θ value conformations thus detected cannot be nearly as accurately quantitated as in NMR experiments, the qualitative predominance of conformations in six-ring hydrazines determined by PE experiments has always agreed with that determined by ^{13}C NMR in solution.[4]

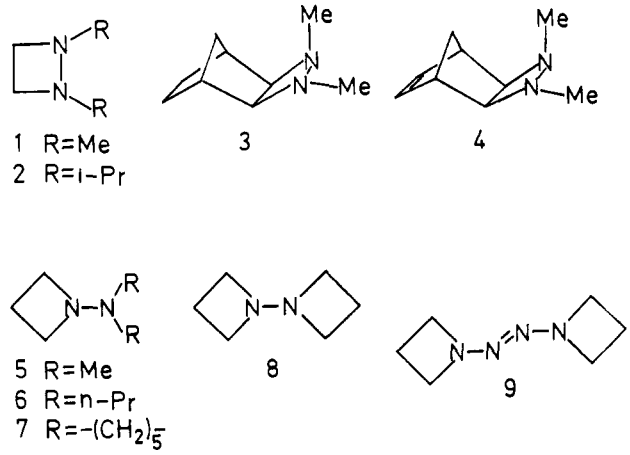
Conformational information on tetraalkylhydrazine radical cations has come almost exclusively from ESR studies,[8] which have established that the barrier for double nitrogen inversion is quite low, and that for some cases in which the planar form is strained, the equilibrium geometry is not planar at nitrogen.

We report here our conformational results on four-membered ring hydrazines and hydrazine radical cations, including both 1,2-dialkyldiazetidines and *N*-aminoazetidines.

Compounds Employed

Diazetidines **1–4** and *N*-aminoazetidines **5–8** were studied. **1** and **2** were prepared in low yield by bisalkylation of the 1,2-dialkylhydrazines with ethylene bromide,[9] and **3** and **4** from the thermal adduct of quadricyclane and diethyl azodicarboxylate.[10a] Reductive alkylation of *N*-aminoazetidine was used to prepare **5–7**, and biazetidine **8** was isolated in disappointingly low yield from the photolysis of 2-tetrazene **9**.

The tosic acid salt of *N*-aminoazetidine was conveniently prepared by catalytic hydrogenation of *N*-nitrosoazetidine in the presence of ferrous sulfate (in our hands lithium aluminum hydride reduction, which works well for the dimethylated system,[10b] gave low yields). To our chagrin, we discovered that workup of the hydrogenation by adding hydrochloric acid before solvent removal caused rearrangement to pyrazolidine hydrochloride. Because use of tosic acid in the workup solves this problem, we presume that 1-protonated 1-aminoazetidine is cleaved by chloride ion to 3-chloropropylhydrazine, which recyclizes at the unsubstituted nitrogen, although this point was not investigated further.



PE Spectroscopic Studies

The positions of the lowest energy ionizations observed are summarized in Table I, and selected spectra are illustrated in Figures 1 and 2. The PE spectrum of **1** was previously reported by Rademacher;[5b] our data are in reasonable agreement. For **2** and **5–8**, three PE peaks were observed in the lone pair region, which requires two conformations with different θ values being significantly populated. As was the case for hexahydropyridazines,[6] the IP_1 peaks for the two conformations overlap and we were unable to deconvolute the first observed PE peak into two peaks in all cases except **5**. The position observed for the first ionization must be dominated by that for the major conformation present, and, although IP_1 for the minor conformation cannot be very different, its value is not known accurately, and is placed in brackets in Table I.

The alkyl substituents in **1** and **2** will be trans to each other, and two trans conformations are available, shown as T_e and T_a. The T_e conformation has the R groups closer to each other, a θ value greater than 120°, and hence a large ΔIP. The T_a conformation has the R groups further apart, a smaller than

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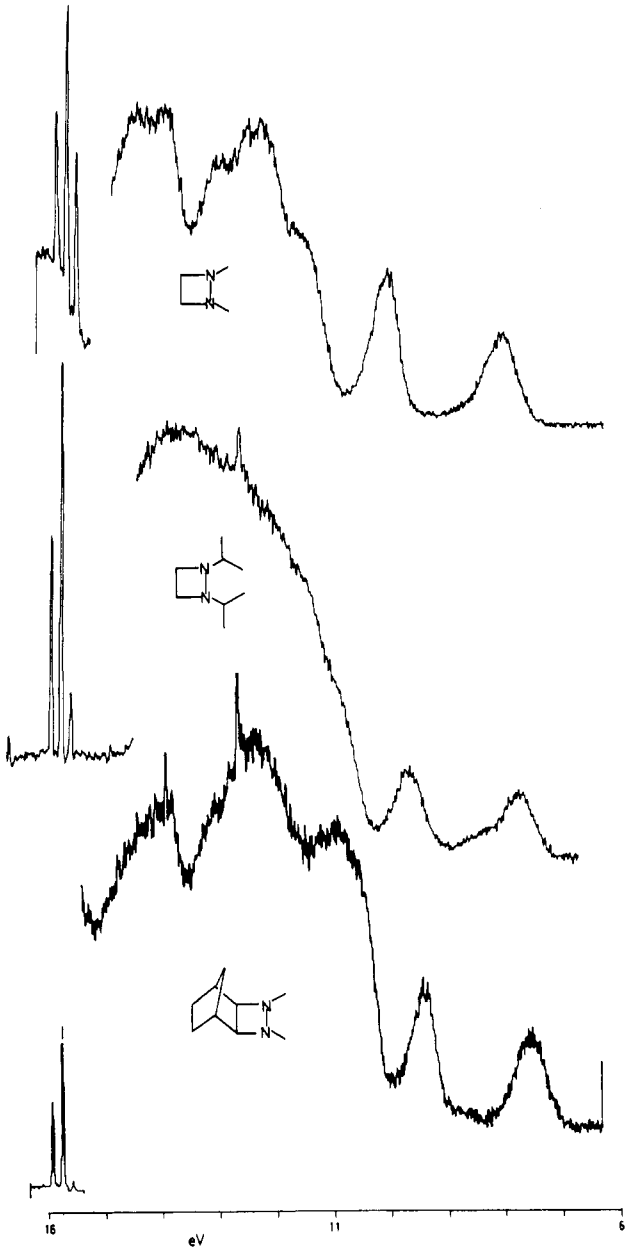


Figure 1. PE spectra of **1, 2,** and **3**. The argon (internal standard) regions are shown at lower gain.

Table I. PE Data for **1–8**

Compd	IP_1, eV	IP_2, eV	ΔIP, eV	Assignment (amount)
1	8.12[a]	10.16[a]	2.04[a]	T_e
2	[7.6]	8.22	[0.6]	T_a (minor)
	7.66	~9.69	~2.02	T_e (major)
3	7.64	~9.52	~1.88	Trans
4	7.68	~9.83[b]	~2.15[b]	Trans
5	8.27	8.94	0.67	Gauche (major)
	7.70	Obsc.	—	Anti (minor)
6	7.54	8.19	0.65	Gauche (major)
	[7.5]	~9.50	[2.07]	Anti (minor)
7	[7.7]	8.35	[0.7]	Gauche (minor)
	7.68	~9.72	~2.04	Anti (major)
8	8.25	8.98	0.73	Gauche (major)
	[8.2]	~10.12	[1.9]	Anti (minor)

[a] Rademacher[5b] reports IP_1 = 7.95, IP_2 = 10.07, ΔIP = 2.12 eV for **1**. [b] A band at 9.04 eV is presumably due to the olefin π ionization. Norbornene IP_1 is at 8.97 eV: P. Bischoff, J. A. Hashmal, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta,* **52,** 1745 (1969).

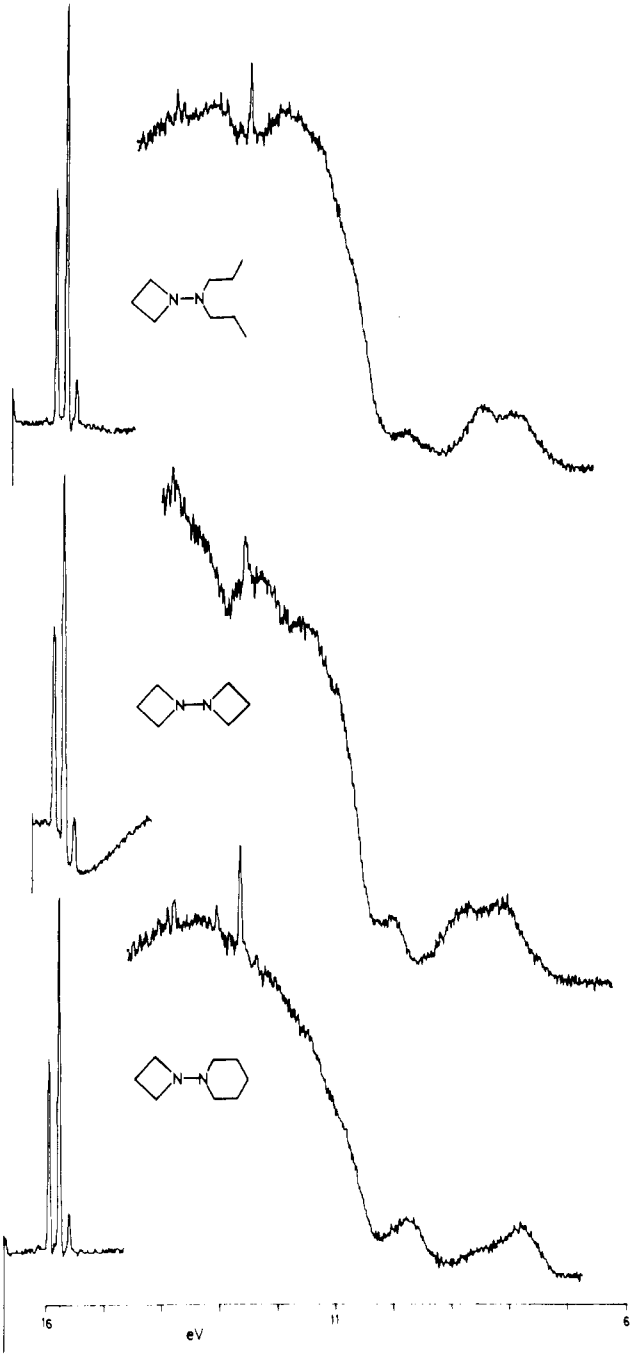
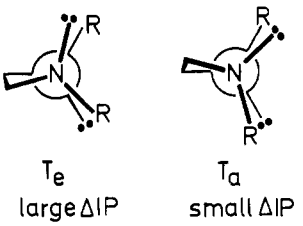


Figure 2. PE spectra of **6, 8,** and **7**.



120° θ value, and a small ΔIP. We find (Table I) that when R = methyl, only the T_e conformation is significantly populated, although when R = isopropyl, a minor amount of T_a is observed. The result that T_a is favored by larger alkyl groups was earlier found for pyrazolidines (five-membered ring hydrazines),[5c] although for pyrazolidines both conformations were detected when R = methyl, but only T_a when R = isopropyl. It is not surprising that the T_e conformation is more predom-

Table II. Activation Parameters for Nitrogen Inversion in 1,2-Diazetidines

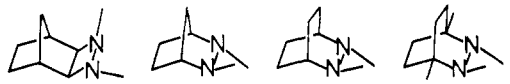
Compd	Solvent	T_c[a]	$\Delta\nu$[b]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}_{298}$, kcal/mol
3	$CFCl_3$	−40	4.8	13.2 ± 0.9	5.2 ± 4.0	11.7 ± 0.3
3	Acetone-d_6	−40	4.3	12.8 ± 0.7	3.2 ± 3.1	11.9 ± 0.2
4	$CFCl_3$	−36	7.7	13.8 ± 0.5	6.7 ± 2.3	11.8 ± 0.2
4	Acetone-d_6	−36	7.7	13.5 ± 0.4	5.3 ± 1.4	11.9 ± 0.1
4	CD_3OD	−45	8.5	12.8 ± 0.3	5.3 ± 1.4	11.2 ± 0.1

[a] Coalescence temperature, °C. [b] Difference in chemical shift of *N*-methyl absorptions, in hertz.

inant for the four-ring than the five-ring example, because the RN,NR steric interaction in T_e is expected to be lowered as the ring is contracted and the nitrogens deviate more from planarity, and the electronic destabilization of T_e should also be lowered by this change. We note that ΔIP is 2.3 eV for T_e dimethylpyrazolidine, compared to 2.0 eV for diazetidines **1** and **2**. For the six-ring case, hexahydropyridazines, T_a has two axial R groups and this conformation is not populated, but even here, larger alkyl groups favor the cis axial, equatorial conformation over T_e. The *R*N,N*R* steric interaction, which is larger in T_e than in T_a, appears to be responsible for the shift from T_e or T_a or axial, equatorial cis conformations when the alkyl group is increased in size.

Hall and Bigard[11] have determined the ^{1}H NMR coupling constants for dimethyl (**1**), diethyl, diisopropyl (**2**), and di-*tert*-butyldiazetidine, concluding that the ring was flatter in **2** than in **1**. Our PE results suggest instead that the coupling constant charges observed are a result of an increasing fraction of the T_a conformation. The T_a and T_e conformations are in rapid equilibrium on the NMR time scale, and averaged couplings will be observed. Their conclusion that di-*tert*-butyldiazetidine is (predominantly) T_a is consistent with our PE result that increasing the size of the alkyl substituents stabilizes T_a relative to T_e, but we unfortunately have no PE data on this compound.

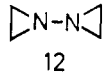
The bicyclic ring of **3** and **4** presumably precludes significant diazetidine ring torsion, and only a single conformation was detected by PE spectroscopy for these compounds, as expected. One might hope that ΔIP for **3** would, then, establish ΔIP for a diazetidine ring with a 0° ring torsion angle. A comparison for ΔIP values for **3** with the five- and six-ring hydrazines **9–11** is shown below. The similarity of ΔIP for **3, 9,** and **10** is prob-



3 9 10 11

ably misleading. We have argued that **10** has significant bicyclic ring torsion from the drop in ΔIP with bridgehead methyl substitution (see **11**).[6c] In these cases, however, significant interaction of the nitrogen lone pair orbitals with the σ orbitals of the hydrocarbon framework seems likely; the "lone pair orbitals" may well have significant σ components. Such mixing is presumably responsible for the surprising change in ΔIP between **3** and **4,** since we doubt that the CN,NC angle can be very different for these two systems—both are constrained to be near 0°. Nevertheless, the larger ΔIP for the T_e conformations of **1** and **2** and substantially smaller ΔIP for the T_a conformation of **2** compared to **3** indicate a substantial degree of diazetidine ring torsion in **1** and **2**. It is likely that the degree of flattening at nitrogen in T_e and T_a conformations is singificantly different, as has been shown to be the case for diequatorial and axial, equatorial six-ring hydrazines.[12]

Rademacher[5] showed that biaziridine **12** exists exclusively

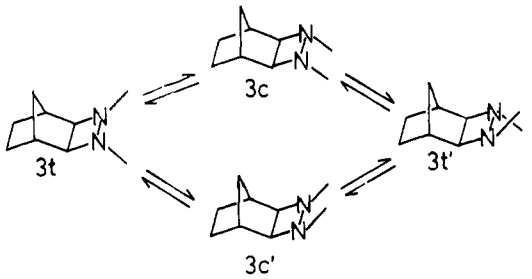


12

in the θ = 180° anti conformation, and observed a large ΔIP of 2.53 eV for **12**. Several *N*-amino five- to seven-ring 1,1-cycloalkylhydrazines exist exclusively in small ΔIP gauche conformations. For *N*-aminoazetidines **5–8,** however, both large and small ΔIP conformations were observed. We assign them to anti and gauche conformations, respectively. The significantly smaller ΔIP values observed for the anti conformations of **6–8** (ca. 1.9 eV) compared to the 2.5 eV for anti **12** is presumably another example of the degree of bend at nitrogen and n,σ interaction influencing ΔIP; the same ΔIP vs. θ curve cannot be used for all hydrazines, especially for strained compounds. Both three- and four-membered 1,1-dialkyl rings favor anti conformations, possibly because there is a greater deformation from planarity at nitrogen in small-ring than larger ring compounds, causing an increased *R*N,N$_2$*R* alkyl,alkyl interaction in the gauche form. We believe that such dialkyl steric interaction is consistent with the observed greater anti content of **7** than **6** or **8**. The equatorial hydrogens of the conformationally rigid piperidine ring of **7** would be expected to have a greater steric interaction with the α-methylene groups of the azetidine ring than would either the *n*-propyl groups of **6** or the second azetidine group of **8,** because both can deform more easily to minimize the steric interaction.

NMR Study of 3 and 4

The separation of ring torsion reversal from nitrogen inversion processes by NMR work is often difficult.[13] The fused-ring systems of **3** and **4** minimize ring torsional effects, and the process by which **3t** is converted to **3t'** is clearly con-



secutive nitrogen inversions, proceeding through **3c** and/or **3c'** as intermediates. Simultaneous inversion at both nitrogens has been correctly argued to be a higher energy process.[14] The cis forms of **3** are both sterically and electronically destabilized relative to the trans forms, and as in other 2,3-dialkyl-2,3-diazabicyclic systems,[14] are not present in detectable concentration. The rate constants for methyl equilibration were determined by computer simulation[15] of the ^{1}H NMR methyl signals at various temperatures. Plots of log (k/t) vs. $1/T$ give straight lines from which the activation enthalpies and entropies of Table II were determined. The activation parameters for **3** and **4** are identical within experimental error, as might have been expected. The positive entropies for nitrogen inversion in these systems are similar in magnitude to those found for nitrogen inversions in other cyclic tetraalkylhydrazines.[13] Small increases in methyl equilibration rate were observed in going from $CFCl_3$ to the more polar solvents acetone and methanol-d_4, possibly resulting from an increase in dipole moment for the transition state for nitrogen inversion com-

pared to the ground state. The increase in rate in methanol-d_4 compared to the nonhydroxylic solvents indicates that methanol hydrogen-bonding effects are not important for this nitrogen inversion.[16]

The $\Delta G^{\ddagger}_{298}$ for methylene equilibration of **1** (which requires double nitrogen inversion) is 15.6 kcal/mol,[11] substantially larger than for double nitrogen inversion for the five-membered ring case, 2,3-dimethyl-2,3-diazabicyclo[2.2.1]heptene, $\Delta G^{\ddagger}_{298}$ = 14.4,[14] or the six-membered ring case, 2,3-dimethyl-2,3-diazabicyclo[2.2.2]octane, $\Delta G^{\ddagger}_{298}$ = 12.3 kcal/mol. The trend toward higher $\Delta G^{\ddagger}$ for nitrogen inversion as ring strain in the planar transition state is increased is well established.[17] Nevertheless, $\Delta G^{\ddagger}_{298}$ for nitrogen inversion is substantially (3.8–3.9 kcal/mol) lower for **3** and **4** than for **1**, despite the fact that all are diazetidines. We presume that ground-state destabilization of **3** and **4** relative to the half-planar transition state is responsible. The tricyclic system both forces the diazetidine ring of **3** and **4** to be eclipsed and causes a steric interaction of one *N*-methyl group with the bridging methylene.

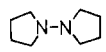
Radical Cation ESR Spectra

The ESR spectrum of $\mathbf{1}^{+\cdot}$ was successfully simulated using the splittings reported in Table III. The assignment of the 15-G splitting to $a(2\mathrm{N})$ was verified by noting that using this assignment, the $\bar{M}_N \pm 0$ lines broaden drastically as the temperature is lowered, until only the $\bar{M}_N = 0$ lines remain observable at −110 °C. It is common for tetraalkylhydrazine radical cations, with their adjacent high spin density $I = 1$ nuclei, to show such extreme anisotropic broadening effects.[8] Also included in Table III are literature splittings[8a] for other tetraalkylhydrazines for comparison. The clear trend of increased splitting when a six ring is contracted to a five ring and further increase with bicyclic fusion apparent in Table III cannot be caused principally by a decreased CNN angle, or $\mathbf{1}^{+\cdot}$ would have had a much higher splitting than that observed. Wood[18] and Krusic[19] have emphasized that the ^{13}C splittings observed for *tert*-butyl radical are time averages over closely spaced thermally available vibrational states, and that it is not useful to think of the amount of bend in most radicals as a static quantity. Their comments apply equally well to $a(\mathrm{N})$ of hydrazine cations, where the ease of bending at nitrogen is probably greater than that of bending at the central carbon of *tert*-butyl radical. The decrease in $a(\mathrm{N})$ for the di-*tert*-butyl compound compared to a tetramethylhydrazine is presumably caused by the increased strain as the nitrogens become nonplanar, causing a steeper energy curve for distortion than for tetramethylhydrazine. Conversely, the large $a(\mathrm{N})$ values for **18** and **19** suggest that the planar form is increased in energy compared to bent forms relative to tetramethylhydrazine, as might be expected from their structures. The decrease in CNN angle necessary in going from **16** to **1** might have been expected to cause a greater equilibrium degree of bend, but this does not result in a higher $a(\mathrm{N})$. We suggest the possibility that the decrease in methyl–methyl interaction in the planar form of $\mathbf{1}^{+\cdot}$ compared to that of planar $\mathbf{16}^{+\cdot}$ compensates for the expected ring-size effect.

The diisopropyl compound $\mathbf{2}^{+\cdot}$ shows decreased nitrogen and methylene splittings compared to $\mathbf{1}^{+\cdot}$. A similar trend was observed in the five-ring analogues $\mathbf{16}^{+\cdot}$ and $\mathbf{17}^{+\cdot}$, although the changes here are smaller, possibly because of larger alkyl–alkyl interaction in nearly planar $\mathbf{17}^{+\cdot}$ compared to $\mathbf{2}^{+\cdot}$.

We have yet to successfully analyze the complex ESR spectra of the unsymmetrical aminoazetidine cations **5–7**, but the spectrum from $\mathbf{8}^{+\cdot}$ is unexpectedly simple. No H_γ splitting was resolved, despite the 0.7–0.8 G H_γ splitting of $\mathbf{16}^{+\cdot}$ and $\mathbf{18}^{+\cdot}$. Because the hyperconjugation contributions of $a(H_\gamma)$ will cancel for the latter two radicals (N_1 and N_2 have opposite coefficients), it appears that the hyperconjugation contribution of $a(H_\gamma)$ in $\mathbf{8}^{+\cdot}$ is similar in size but opposite in sign to that of the other contributions, resulting in a small $a(H_\gamma)$. The nitrogen splittings for $\mathbf{1}^{+\cdot}$ and $\mathbf{8}^{+\cdot}$ are about the same size, although dimethylpyrazolidine cation $\mathbf{16}^{+\cdot}$ has a rather larger nitrogen splitting than that of bispyrrolidine, $\mathbf{20}^{+\cdot}$. We suggest that $\mathbf{20}^{+\cdot}$ lacks a significant RN_1N_2R interaction which is present for $\mathbf{16}^{+\cdot}$, causing a greater average deformation from planarity in the monocyclic cation, and the observed increase in $a(\mathrm{N})$. Such an RN_1N_2R interaction should be less important in $\mathbf{1}^{+\cdot}$, damping the effect.

Table III. ESR Splitting Constants (G) for Some Tetraalkylhydrazines Cation Radicals[a]

Compd		$a(2\mathrm{N})$	$a(\mathrm{NC}H_2$ ring)	Other splittings
	**1**[b]	15.0	15.7 (4 H)	13.1 (6 H)
	**2**[c]	13.8	15.5 (4 H)	5.7 (2 H)
	**13**	~11.9		~11.9 (6 H)
	**14**	13.1	14.2 (4 H)	12.5 (5 H)
	**15**	13.4		12.7 (10 H)
	**10**	13.9		12.7 (6 H)
	**16**	15.0	14.0 (4 H)	12.8 (6 H) 0.7 (2 H_γ)
	**17**	~14.2	~14.2 (4 H)	4.6 (2 H)
	**9**	16.0		13.1 (6 H)
	**18**	17.6	15.6 (8 H)	0.8 (4 H_γ)
	**19**	18.8		12.8 (6 H)
	**8**[d]	14.8	17.2 (8 H)	
	**20**	12.9	18.5 (8 H)	0.3 (8 H_γ)

[a] From ref 8a, except where noted. [b] In butyronitrile containing 0.1 M *n*-Bu_4NClO_4, intramuro electrolytic generation, recorded at 25 °C. [c] In butyronitrile, generated by reaction with tris-*p*-bromophenylaminium hexachloroantimonate, recorded at −37 °C. [d] As *c*, at 25 °C.

Experimental Section

1,2-Dimethyl-1,2-diazetidine (1).[9] A mixture of 2.0 g (33 mmol) of 1,2-dimethylhydrazine, 25 mL of *o*-xylene, and 7.5 g of anhydrous sodium carbonate was stirred at 100 °C while 6.25 g (33 mmol) of 1,2-dibromoethane in 10 mL of *o*-xylene was added over a 1-h period. After 30 min of additional heating, 20 mL of distillate was collected by slow distillation. The top layer of the two-phase distillate was separated and dried over sodium sulfate. **1** was isolated by VPC in 4.9% yield, but contained formaldehyde imine trimer as an impurity. For **1**: NMR ($CDCl_3$) δ 3.51 (m, 2 H), 3.00 (m, 2 H), 2.45 (s, 6 H); IR no NH or C=O; empirical formula established by high-resolution mass spectroscopy.

1,2-Diisopropyl-1,2-diazetidine (2). A mixture of 3.0 g (27 mmol) of 1,2-diisopropylhydrazine, 5.13 g (27 mmol) of 1,2-dibromoethane, 2.86 g of sodium carbonate, and 200 mL of 50% ethanol was refluxed for 48 h. After cooling, 100 mL of concentrated HCl was added, solvent removed at reduced pressure, and the residue dissolved in concentrated sodium hydroxide. Ether extraction gave a fraction boiling at 75–91 °C (20 mm), from which **2** was isolated in 2.2% yield by VPC. NMR (acetone-d_6) δ 3.4 (m, 2 H), 3.1 (m, 2 H), 2.78 (hept, 2

H), 0.91 (d, 12 H); IR no NH or C=O; empirical formula established by high-resolution mass spectroscopy.

3,4-Dimethyl-3,4-diazatricyclo[4.2.1.0^{2,5}]non-7-ene (4) was prepared by dropwise addition of 2.0 g (7.5 mmol) of the quadricyclane-diethyl azodicarboxylate adduct[10a] in 19 mL of anhydrous ether to a well-stirred mixture of 0.76 g (20.9 mmol) of lithium aluminum hydride in 40 mL of ether. After stirring at room temperature for 2 h, the excess hydride was destroyed with saturated aqueous ammonium chloride, the liquid decanted and dried over magnesium sulfate, and the solvent distilled. Distillation of the oily residue at 55–60 °C (3 mm) gave 0.58 g (52%) of **4** as a colorless oil: NMR ($CFCl_3$) δ 6.03 (m, 2 H), 3.55 (broad s, 2 H), 2.97 (broad s, 2 H), 2.45 (s, 6 H), 2.35–2.58 (m, 1 H), 1.45–1.65 (m, 1 H); IR no NH or C=O; empirical formula $C_9H_{14}N_2$ established by high-resolution mass spectroscopy.

3,4-Dimethyl-3,4-diazatricyclo[4.2.1.0^{2,5}]nonane (3) was prepared in 60% yield by the method used for **4**, starting with the hydrogenated quadricyclane-diethyl azodicarboxylate adduct:[10a] bp 45–50 °C (1 mm); NMR ($CFCl_3$) δ 3.40 (broad s, 2 H), 2.55–2.70 (m, 1 H), 2.28 (broad s, 2 H), 0.90–1.60 (m, 5 H); IR no NH or C=O; empirical formula established by high-resolution mass spectroscopy.

Tosic Acid Salt of *N*-Aminoazetidine. *N*-Nitrosoazetidine, (3.0 g, 36 mmol) 2.0 g of 5% Pd/$CaCO_3$, and 0.62 g of ferric sulfate heptahydrate were dissolved in a deaerated mixture of 150 mL of ethanol and 600 mL of water. The mixture was hydrogenated at an initial hydrogen pressure of 3 atm in a Parr shaker until the calculated amount of hydrogen was taken up (about 30 min). After addition of 36 mmol of tosic acid hydrate, the catalyst was filtered and the solvent evaporated. The remaining salts were used directly in the following procedures.

1-Dimethylaminoazetidine (5). The tosic acid salt obtained by hydrogenation of 2.9 g (34 mmol) of *N*-aminoazetidine, 1.36 g (34 mmol) of sodium hydroxide, 50 mL of methanol, 14.3 mL (200 mmol) of formalin, and 4.26 g (68 mmol) of sodium cyanoborohydride were stirred under nitrogen while acetic acid was added dropwise until the solution registered pH 6 on pHydrion paper. After stirring for 20 h, an excess of tosic acid was added and the solution evaporated to dryness. The salts were dissolved in concentrated sodium hydroxide and extracted with methylene chloride, and the organic layer was dried with sodium sulfate. After distillation of most of the solvent, **5** was isolated in 1.8% yield by VPC: NMR ($CDCl_3$) δ 3.28 (t, 4 H), 2.27 (s, 6 H), 1.90 (quintet, 2 H); IR no NH or C=O; empirical formula established by high-resolution mass spectroscopy.

1-Dipropylaminoazetidine (6). The same method was used as for **5**, employing 2.0 g (23 mmol) of 1-nitrosoazetidine and 7.0 g (120 mmol) of propanal. Workup was accomplished by adding 50 mL of 15% sodium hydroxide and extraction with pentane. After distillation of the pentane, **6** was isolated by distillation: bp 116–119 °C (1 atm); 1.38 g (38%); NMR ($CDCl_3$) δ 3.36 (t, 4 H), 2.50 (t, 4 H), 1.86 (quintet, 2 H), 1.34–1.66 (m, 4 H), 0.91 (t, 6 H); IR no NH or C=O; empirical formula established by high-resolution mass spectroscopy.

1-(1-Piperidinyl)azetidine (7). The same procedure was employed as for **5**, using 2.0 g (23 mmol) of 1-nitrosoazetidine, 9.2 g (23 mmol) of 25% aqueous glutaraldehyde, and 1.0 g (15 mmol) of sodium cyanoborohydride. After basicification, pentane extraction gave 0.25 g (8%) of crude **7**, which was purified by VPC: NMR ($CDCl_3$) δ 3.52 (t, 4 H), 2.66 (t, 4 H), 2.00 (quintet, 2 H), 1.2–1.9 (m, 6 H); IR no NH or C=O; empirical formula established by high-resolution mass spectroscopy.

Azoazetidine (9). To the tosic acid salts obtained by hydrogenation of 3.2 g (37 mmol) of 1-nitrosoazetidine were added 40 mL of 5 M hydrochloric acid cooled to −10 °C and 50 mL of 1.0 N $KBrO_3$ cooled to 0 °C over a period of 1 min, keeping the solution below 0 °C.[21] Sodium hydroxide (40 mL, 15%) cooled to 0 °C was added immediately, and the solution extracted with pentane. Solvent removal and crystallization from pentane gave 1.0 g of **9** (38%): mp 53–55 °C; NMR ($CDCl_3$) δ 3.81 (t, 8 H), 2.16 (quintet, 2 H); IR no NH or C=O; empirical formula established by high-resolution mass spectroscopy.

1,1′-Biazetidine (8). A solution of 0.5 g (3.6 mmol) of **9** in 280 mL of pentane was irradiated with a 450-W Hanovia lamp until **8** was 95% decomposed (determined by VPC) and concentrated by distillation. **8** was isolated by VPC: 20 mg (4.9%); NMR ($CDCl_3$) δ 3.30 (t, 8 H), 1.86 (quintet, 4 H); IR no NH or C=O; empirical formula determined by high-resolution mass spectroscopy.

NMR Studies. Freshly distilled biazetidine (60 mg) was dissolved in 0.5 mL of the appropriate solvent containing tetramethylsilane as internal standard and 40 μL of dichloromethane as an internal lock; the resulting solution was sealed in a medium-walled 5-mm NMR tube. Variable-temperature NMR spectra were recorded on a Varian T-60 NMR spectrometer equipped with a variable-temperature probe and Perma-Lock. Temperatures were determined to ±1 °C with a Thermo-Electric Minimite, and frequencies were measured with a Monsanto Counter-Timer frequency counter.

Rate constants (k) were determined above and below the coalescence temperature by spectral simulation of *N*-methyl absorptions using the DNMR/3 program of Binsch and Kleier.[15] Simulated spectra were plotted on a Hewlett-Packard 7200A plotter and were compared visually with experimental spectra. Activation parameters and associated standard deviations were determined by linear least-squares analyses of plots of log (k/t) vs. $1/T$.

Corrections for the transverse relaxation time were made as a function of temperature;[22] a transmission coefficient[14] of $\frac{1}{2}$ was used in determination of the activation parameters.

The PE[6] and ESR[8] equipment and techniques employed have been previously described.

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