INDO calculations suggest that spin density is higher on the acylated nitrogen than on the alkylated nitrogen of unsymmetrically acylated hydrazine radical cations.

These results greatly increase both the available potential range and structural diversity of amino nitrogen compounds which give long-lived radical cations. The only such compounds previously reported to have $E°'$ above 1 V vs. SCE were protected chloro amines. The study of conformational effects on both $E°'$ and cation-radical lifetime for acylated hydrazines should prove important in considering how conformation affects reactivity.

Experimental Section

The methods used to prepare **7**–**9** and **13**,[5] **10** and **11**,[20] **12**, **14**, **17**, and **18**,[21] **15**,[22]a **16** and **20**,[22b] and **19**[23] have been previously published.

9-Phthalimido-9-azabicyclo[3.3.1]nonane (21) was prepared by refluxing equimolar amounts of 9-amino-9-azabicyclo[3.3.1]nonane, **1**-(NH_2),[24] and phthalic anhydride in benzene with a water separator for 10 h, removal of solvent, and sublimation to give **21** as a colorless solid, mp 118 °C, in 88% yi eld: ^1H NMR (acetone-d_6) δ 1.4–2.4 (complex, 12 H), 3.1 (br s, 2 H), 7.5 and 7.9 (2 m, 4 H). The empirical formula was established by high resolution mass spectroscopy.

Cyclic voltammetry[25] and ESR[26] experiments were conducted as previously described. INDO and CNDO calculations were performed on a Harris/7 computer, using program BONDO.[8]

Acknowledgment. We thank the National Science Foundation for partial financial support of this work under Grant CHE 8026111. We thank Professor F. A. Weinhold of this department for patient instruction in the use of BONDO and helpful discussion.

Registry No. 1 (NH_2), 4390-44-7; **7**, 72282-78-1; **8**, 23292-39-9; **9**, 72282-77-0; **10**, 78790-57-5; **11**, 10316-53-7; **12**, 3310-58-5; **13**, 72282-81-6; **13**$^{+\cdot}$, 84960-96-3; **14**, 3310-59-6; **15**, 3661-10-7; **16**, 22527-64-6; **17**, 35691-30-6; **18**, 52944-50-0; **19**, 3645-44-1; **20**, 4770-30-3; **21**, 84960-95-2; phthalic anhydride, 85-44-9; formylhydrazine radical cation, 84960-97-4; *N*,*N*-diformylhydrazine radical cation, 84960-99-6.

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Comparison of Free Energy Changes for Nitrogen Inversion and Electron Loss for Some Amino Nitrogen Compounds

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Contribution from the Samuel M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received September 1, 1982*

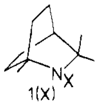
Abstract: 2-Chloro-1,3,3-trimethyl-2-azabicyclo[2.2.2]octane [**1**(Cl)] was found by ^{13}C NMR to have a $\Delta G^{\ddagger}_N$ (−95 °C) of 7.57 (3) kcal/mol and 9-chloro-9-azabicyclo[3.3.1]nonane [**4**(Cl)] a $\Delta G^{\ddagger}_N$ (+35 °C) of 14.24 (5) kcal/mol. The $E°'$ for **1**(Cl) in acetonitrile is +1.25 V vs. SCE and its vertical first ionization potential 8.10 eV. $E°'$ for 3,3-dimethyl-2-azabicyclo-[2.2.2]octanyl-2-oxy [**2**(O·)] is +0.56 V. Comparison of $E°'$ values for **1**(X), **2**(X), and 2-azabicyclo[2.2.2]octane derivatives **3**(X) and **4**(X) with X = O·, N=]$_2$, and Cl are made. Larger changes in $E°'$ with bicyclic alkyl group changes are seen when $\Delta G^{\ddagger}_N$ for the neutral compound is larger, and the implications of this fact are discussed. The irreversible E_p^{ox} values for the corresponding methylamines reflect the same trends as the alkyl groups are changed.

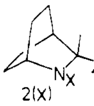
Large changes in geometry at nitrogen frequently accompany electron loss from amino nitrogen compounds R_2NX. Nitrogen prefers to be pyramidal in the neutral form but planar in the radical cation. Strain energy differences resulting from these geometrical preferences must show up in the free energy of electron loss, $\Delta G°_e$. Changes in $\Delta G°_e$ in a series of R_2NX compounds are usually measurable only if $(R_2NX)^{+\cdot}$ is long-lived under the conditions of a cyclic voltammetry (CV) experiment. Cation radical lifetimes of tens of milliseconds are required, and the factor limiting lifetime appears to usually be deprotonation of the radical cation by the neutral form. Tetraalkylhydrazines (X = NR_2) and tetraalkyltetrazines (X = (—N=N—NR_2)) give long-lived radical cations for most R groups, but when X is less cation stabilizing, the radical cations usually decompose rapidly on the CV time scale. "Bredt's rule kinetically protected" bicyclic dialkyl amino groups, in which the hydrogens on carbons attached to nitrogen are held close to the nodal plane of the half-filled nitrogen p orbital of the cation radical, turn out not to deprotonate on the CV time scale for many X groups.[1] This allows $\Delta(\Delta G°_e)$ measurements to be made for a wider variety of compounds than when R groups which have α-hydrogens which can be lost rapidly are present.

In this work changes in the free energy for electron loss, $\Delta(\Delta G°_e)$ values, for four bicyclic R_2N groups having three relatively small X groups are compared. Because flattening at nitrogen occurs in both electron loss and nitrogen inversion, it is suggested that comparing $\Delta(\Delta G°_e)$ with changes in the activation energy for nitrogen inversion, $\Delta(\Delta G^{\ddagger}_N)$, for different R_2N groups is useful.

Results

The compounds considered in this paper are derivatives of bicyclic amines **1**(H)–**4**(H). The derivatives considered are


1(X)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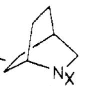
3(X)


4(X)

chloramines (X = Cl), symmetric 2-tetrazenes (designated as X = N=]$_2$; see the example below), nitroxides (X = O·), and me-

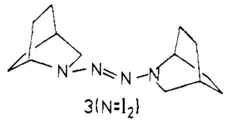
3(N=]$_2$)

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Table I. Cyclic Voltammetry Data for Some Bicyclic Amine Derivatives[a]

compound	R_2N=**1**	R_2N=**2**	R_2N=3	R_2N=**4**
R_2NCl	1.25 (0.080)	1.29 (0.069)[b]	$E_p^{ox} = 1.32$	1.49 (0.082)[b]
$R_2N-N=]_2$		0.17 (0.071)[b]	0.29 (0.063)[b]	0.40 (0.072)[b]
$R_2NO\cdot$	0.51 (0.073)[c]	0.56 (0.068)		0.58 (0.072)[c]
R_2NMe		$E_p^{ox} = 0.59$	$E_p^{ox} = 0.68$	$E_p^{ox} = 0.76$

[a] Values quoted are $E°'$ (ΔE_{pp}) in V vs. SCE for electrochemically reversible electron transfers, and the entries designated E_p^{ox} refer to oxidation peak potentials. All entries refer to CV experiments conducted at 200 mV/s scan rates. Conditions: ca. 1 mM substrate in acetonitrile containing 0.1 M n-Bu_4NClO_4; gold electrode except for the chloroamines, where a platinum electrode was employed. [b] From ref 2. [c] From ref 3. $E°'$ for 1 (X = O·) was determined as 0.51_5. A redetermination at the same time as **2** (X = O·) was run gave 0.50_8, so 0.51 was used.

Table II. Dynamic ^{13}C NMR Inversion Barrier Data[a] for Chloramines **1**(Cl) and **4**(Cl)

	1(Cl)	**4**(Cl)
temperature range	−128 to −76	−17 to +76
solvent	1:1 CD_2Cl_2-CF_2Cl_2	$CDCl_3$
data points	9	13
$\Delta G^{\ddagger}$, kcal/mol [T_c, °C]	7.57 (3) [−95]	14.24 (5) [+35]
$\Delta H^{\ddagger}$, kcal/mol	7.9 (2)	14.8 (5)
$\Delta S^{\ddagger}$, eu	+1.7 (13)	+1.7 (18)
$\Delta G^{\ddagger}$ [25 °C]	7.36 (17)	14.26 (5)

[a] Numbers in parentheses refer to statistical error in the last place quoted and are included only for comparison purposes.

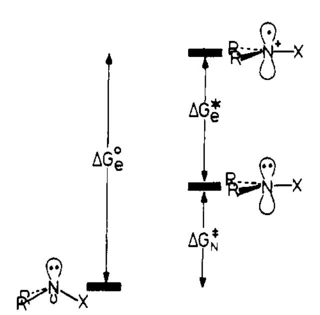

Figure 1. Diagram showing the relationship in free energy between a neutral R_2NX compound, its transition state for nitrogen inversion, and its radical cation.

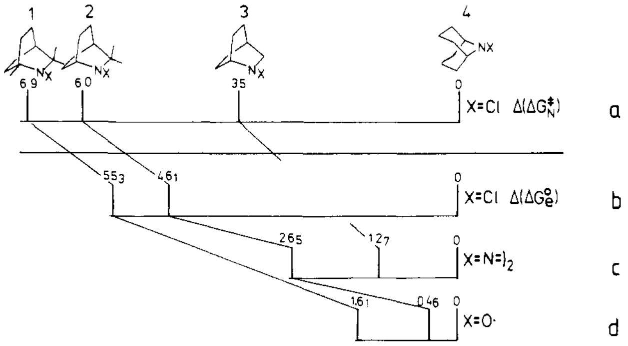

Figure 2. Comparison of changes in $\Delta G^{\ddagger}_N$ of chloramines (a) and changes in ease of oxidation for chloramines (b), 2-tetrazenes (c), and nitroxides (d). The numbers are in kcal/mol relative to the **4**(X) compound.

thylamines (X = CH_3). Of the 16 compounds in this series, the nitroxide **3**(O·) was not studied because it is known to be too unstable for isolation, and both **1**(Me) and **1**(N=]$_2$) remain unprepared. The formal potentials $E°'$ for the examples which undergo electrochemically reversible oxidation, along with the oxidation peak potentials for the electrochemically irreversible examples, the N-methylamines and the "unprotected" chloramine **3**(Cl), appear in Table I. Several entries are from previous papers.[2,3] Dynamic ^{13}C NMR experiments gave nitrogen inversion barrier data for **1**(Cl) and **4**(Cl), and the results are reported in Table II. The $\Delta G^{\ddagger}$ [T_c] values observed for **4**(Cl) lie near the middle of the 14 ± 1 kcal/mol range estimated by Lehn from ^1H NMR data.[4] Nitrogen inversion barriers determined in the same fashion have been previously reported for chloramines **2**(Cl) and **3**(Cl)[2] and methylamines **3**(Me)[5] and **4**(Me),[6] while that for **2**(Me) proved to be too low for its observation by ^{13}C NMR.[2] Experimental inversion barriers have not to our knowledge yet been reported for any 2-tetrazenes or nitroxides.

Discussion

General Trends in R_2NX Oxidation Potentials. Differences in the ease of electron removal from various tetraalkylhydrazines have received a great deal of study. Alkyl group structural changes which raise $\Delta G^{\ddagger}_N$ sometimes make electron removal more difficult, but the sensitivity of $\Delta G^{\ddagger}_N$ to the NN rotational angle[7] and the different NN rotational angle preference for neutral hydrazines and their radical cations[8] cause many exceptions to such a trend. The principal factor causing changes in ΔG°_e for tetraalkylhydrazines has been argued to be different steric strain energies for the neutral and cationic forms.[8]

The X groups studied here have been chosen to have effective cylindrical symmetry about the NX bond (X = Cl, O·, CH_3; 2-tetrazenes will be discussed later), so that NX rotation effects are eliminated. For these compounds, we suggest it is useful to consider the energy diagram of Figure 1. The adiabatic electron loss (free energy change ΔG°_e) can be mentally broken up into flattening at nitrogen (free energy change $\Delta G^{\ddagger}_N$) and a nearly vertical electron loss (free energy change labeled ΔG^{*}_e). We expect that steric changes which affect ΔG°_e when the structure of R_2N is changed, such as RX nonbonded interaction changes and the effects of RNR angle changes, should virtually completely also occur in $\Delta G^{\ddagger}_N$, allowing these effects to be "factored out" of ΔG°_e. The residual free energy change ΔG^{*}_e is an essentially vertical electron loss. Although ΔG^{*}_e cannot be directly measured because the starting structure is an energy maximum and hence not present in solutions of R_2NX, one ought to be able to use experiments on other vertical ionization processes to predict how ΔG^{*}_e will change for various R_2N groups. It is known that for simple alkyl groups, vertical ionization potentials decrease in the order methyl > primary > secondary > tertiary. It is also known that the range of such effects decreases a great deal in solution, because alkyl group polarizability effects nearly disappear. For tetraalkylhydrazines, it has been shown that the effect of lengthening primary alkyl groups on $\Delta(\Delta G^{\circ}_e)$ is rather small but measurable at the 0.2 kcal/mol resolution of $E°'$ measurements.[8] Vertical ionization potentials for the chloramines studied here, **1**(Cl) **2**(Cl), **3**(Cl), and **4**(Cl), are 8.10 (reported here), 8.34, 8.57, and 8.55 eV,[2] respectively. The loss of polarizability effects and sensitivity of IP_1 to bending at nitrogen[2] make direct comparison of vapor-phase and solution experiments difficult, but these IP_1 values support the idea that increased branching makes ionization easier in these bicyclic R_2N groups.

Throughout this paper, we will only consider differences in the ease of oxidation as R_2 in R_2NX is changed. These differences are displayed visually in Figure 2, where differences between $E°'$ for **4**(X) and the other bicyclic alkyl groups studied are shown

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(6) Nelsen, S. F.; Weisman, G. R. Clennan, E. L.; Peacock, V. E. *J. Am. Chem. Soc.* **1976**, *98*, 6893.

(7) Nelsen, S. F. *Acc. Chem. Res.* **1978**, *11*, 14.

(8) Nelsen, S. F. *Acc. Chem. Res.* **1981**, *14*, 131.

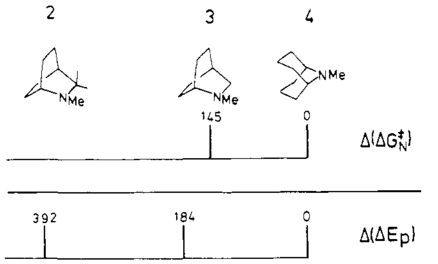

Figure 3. Comparison of changes in $\Delta G^{\ddagger}{}_{N}$ for methylamines with changes in oxidation peak potentials, expressed in kcal/mol.

converted to kcal/mol on a different horizontal axis for each X. The entry for **4**(X) in each case therefore comes at 0 kcal/mol. Because oxidation is easier for the other three bicyclic R_2N groups studied, the entries for these compounds appear to the left of the **4**(X) compound in each case. Because the 2-tetrazenes have two nitrogens which flatten upon electron removal, $\Delta E^{\circ\prime}$ was divided by 2 before converting it to kcal/mol. For the methylamines, irreversible oxidation was observed, so $E^{\circ\prime}$ could not be measured. Figure 3 is a plot of differences in $E_p{}^{ox}$ values, displayed in exactly the same way as the $E^{\circ\prime}$ values were in Figure 2.

Examination of Figures 2 and 3 shows that the differences in ease of oxidation decrease in the order X = Cl > Me > N=]$_2$ > O·. Because the nitrogen inversion barriers decrease in this order, we conclude that $\Delta G^{\ddagger}{}_{N}$ is a major component of the oxidation potential of R_2NX compounds. The remainder of this paper will consist of examining the numbers which appear in Figures 2 and 3 to see if they are useful in understanding the processes of electron removal and nitrogen inversion.

$\Delta(\Delta G^{\ddagger}{}_{N})$ and $\Delta(\Delta G^{\circ}{}_{e})$ for Nitroxides and 2-Tetrazenes. It seems most useful to start by considering the nitroxide data of Figure 2d. Rassat and co-workers[9] have shown that nitrogen inversion in **1**(O·) and **4**(O·) is fast on the ESR time scale, even at low temperatures. They point out the electronic analogy between the three electron π systems of nitroxides and formaldehyde electronically excited states which are believed to be comparably bent at carbon to the bend of nitroxides at nitrogen and which have inversion barriers estimated to be under 1 kcal/mol. They also refer to ab initio calculations on H_2NO· which give an inversion barrier under 0.1 kcal/mol. If nitroxides have a very low $\Delta G^{\ddagger}{}_{N}$, $\Delta(\Delta G^{\ddagger}{}_{N})$ for different nitroxides is even smaller. To a good degree of approximation, then, the $\Delta(\Delta G^{\ddagger}{}_{N})$ term should drop out completely for nitroxides, making the $\Delta(\Delta G^{\circ}{}_{e})$ observed a good measure of $\Delta(\Delta G^{*}{}_{e})$. The ditertiary nitroxide **1**(O·) is 1.6 kcal/mol thermodynamically easier to oxidize than is **4**(O·), while the secondary, tertiary **2**(O·) is 0.5 kcal/mol[10] easier (Figure 2d). The order of $E^{\circ\prime}$ values observed is that expected, more branched alkyl groups causing lower $E^{\circ\prime}$. If nitroxides **2**(O·) and **4**(O·) do have an inversion barrier difference, their $E^{\circ\prime}$ values prove it cannot be very large. The observed $\Delta G^{\circ}{}_{e}$ difference is only 0.5 kcal/mol, and we will assume it is completely caused by $\Delta(\Delta G^{*}{}_{e})$.

Turning to the 2-tetrazene data of Figure 2c, their $\Delta(\Delta G^{\circ}{}_{e})$ values lie between those of the nitroxides and the chloramines. Although the 2-tetrazene "X" group of R_2NX is not cylindrically symmetrical, both vapor-phase photoelectron spectroscopic[11,12] and solid-state X-ray crystallographic[13] data show that the terminal nitrogen lone pair orbital axis is coplanar with the adjacent sp^2 nitrogen π axis. Because the radical cation has the same N_1N_2 (and N_3N_4) rotational angle preference to maintain delocalization of the positive charge, and the R_2N groups are far enough apart that steric interaction between them is insignficant,[14] 2-tetrazenes fit the arguments used in constructing Figure 1. $\Delta(\Delta G^{\circ}{}_{e})$ for **2**(N=]$_2$) is 2.6_5 kcal/mol, which would only occur if there were a significant $\Delta G^{\ddagger}{}_{N}$ difference for **2**(N=]$_2$) and **4**(N=]$_2$). Because the formal increase in positive charge at N in a 2-tetrazene when an electron is removed is slightly less than 0.5 (tetramethyltetrazene has a terminal nitrogen ESR splitting 84% as large as that of tetramethylhydrazine[8]), we expect $\Delta(\Delta G^{*}{}_{e})$ to be no larger in a 2-tetrazene than in a nitroxide. When the same $\Delta(\Delta G^{*}{}_{e})$ is used for **2**(N=]$_2$) as for **2**(O·), the difference in inversion barrier at N of **2**(N=]$_2$) and **4**(N=]$_2$) is about 2.1_5 kcal/mol. To estimate how high $\Delta G_{N}{}^{\ddagger}$ might be, we will make the assumption that $\Delta(\Delta G^{\ddagger}{}_{N})$ using other bicyclic alkyl groups will be proportional to $\Delta G^{\ddagger}{}_{N}$ for **4**(X). Some data are available to test this assumption. $\Delta G^{\ddagger}{}_{N}$ for **4**(Cl) is 14.2_4 kcal/mol, and $\Delta(\Delta G^{\ddagger}{}_{N})$ of **3**(Cl) is 3.5 kcal/mol. $\Delta G^{\ddagger}{}_{N}$ of **4**(Me) is 7.1 kcal/mol, 50% that of **4**(Cl), and $\Delta(\Delta G^{\ddagger}{}_{N})$ of **3**(Me) is 1.4_5 kcal/mol, 41% that of the chloramine. The proportionality we assume, then, is experimentally approximately true for **3**(X) and **4**(X) with X = Cl and CH_3. Because $\Delta(\Delta G^{\ddagger}{}_{N})$ of **2**(Cl) is 6.0 kcal/mol, a 2.1_5 $\Delta(\Delta G^{\ddagger}{}_{N})$ for **2**(N=]$_2$) places $\Delta G^{\ddagger}{}_{N}$ of **4**(N=]$_2$) at about 14.2_4 $(2.1_5/6.0)$ or 5 kcal/mol. This is too low for measurement by ^{13}C NMR, particularly considering the low solubility of **4**(N=]$_2$). A second estimation of $\Delta G^{\ddagger}{}_{N}$ of **4**(N=]$_2$) ought to be available from the comparison of $E^{\circ\prime}$ values for tetrazenes **3** and **4**. We lack, however, an experimental value for the solution vertical ionization difference represented by $\Delta(\Delta G^{*}{}_{e})$ because **3**(O·) is unisolable. Because **3** has primary, secondary alkyl groups and **4** two secondary ones, $\Delta G^{*}{}_{e}$ should be slightly larger for **3** than for **4**, and $\Delta(\Delta G^{\circ}{}_{e})$ should be slightly negative. Using a value of −0.2 kcal/mol lowers to a **4**(N=]$_2$) inversion barrier estimate of 14.2_4 $(1.4_7/3.5)$ = 6.0 kcal/mol. This number is encouragingly close to the 5.0 kcal/mol arrived at above by comparing the $E^{\circ\prime}$ values of **2**(N=]$_2$) and **4**N=]$_2$), considering reasonable estimation of the probable error of the comparisons.

Inversion Barriers and Bending at N in Conjugated Amines. We now consider what is know about conjugated amine inversion barriers and amounts of bend at N, in an attempt to decide whether a $\Delta G^{\ddagger}{}_{N}$ of 5 kcal/mol for **4**(N=]$_2$) is believable. Experimental inversion barrier estimations for conjugated amines come principally from detailed analyses of microwave and IR spectra. Lehn's review[4] quotes work on formamide (H_2NCHO), cyanamine (H_2NCN), aniline ($H_2NC_6H_5$), and nitroamine (H_2NNO_2) which yielded bending angles β (NX bond, NH_2 plane dihedral angles, β = 0° for planar N and 54.7° for tetrahedral N) of 17, 38, 39, and 51°, respectively. We prefer to discuss the average of the three bond angles at N (α_{α} = 120° for planar N and 109.5° for tetrahedral N) because its changes are more nearly linear with percent p hybridization changes and hence with energy changes. Changes in β are very nonlinear with energy; large β changes near β = 0° cost very little energy. The α_{av} values for the series above are 118.9, 115.0, 114.8, and 110.9°, respectively. The N inversion barriers were estimated at 1.1, 1.9–2.0, 2.0, and 2.7 kcal/mol, respectively.[4] More recently, however, Hansen and co-workers[15] have argued that the microwave spectrum of formamide was misinterpreted and that it as well as other amides are really planar at N but have low energies for the out-of-plane bend at N. They suggest that only a 0.5 kcal/mol input in energy might bend acetamide to β as large as 40°, although they reference ab initio calculations that give a rather stiffer planar structure,[16] 0.5 kcal/mol of energy only increasing β to 5–10°. In contrast, further work on the aniline microwave spectrum has changed β little, only

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[9] (a) Rassat, A.; Rey, P. *Tetrahedron* **1973**, *29*, 1599. (b) Dupeyre, R. M.; Rassat, A. *Ibid.* **1978**, *34*, 1501.

[10] We previously pointed out (ref 2, footnote 11) that removal of a second electron from a 2-tetrazene radical cation should not involve a flattening term and ought to depend principally upon what is here called $\Delta G^{*}{}_{e}$. Comparing first and second oxidation $E^{\circ\prime}$ values of **2**(O·) and **4**(O·) gave a $\Delta(\Delta G^{*}{}_{e})$ of 2.5 kcal/mol per substitution of **2** for **4**. This is considerably larger than the 0.5 kcal/mol obtained here from nitroxide data. Exactly why the discrepancy arises is unclear. We suggest that 0.5 kcal/mol figure is more consistent with the rest of our data.

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[13] Unpublished results from the groups of V. J. Day and C. R. Michejda. We thank Dr. Michejda for private communication of these results.

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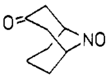
[15] Hansen, E. L.; Larsen, N. W.; Nicolaisen, F. M. *Chem. Phys. Lett.* **1980**, *69*, 327.

[16] Kimkowski, V. J.; sellers, H. L.; Schäfer, L. *J. Mol. Struct.* **1979**, *54*, 299.

to $\beta = 37.5 \pm 2°$ (α_{av} 115.0°)[17] in one analysis, and recent inversion barrier estimations include 1.5 kcal/mol ($\beta = 42.17°$)[18] and 1.3 kcal/mol ($\beta = 42°$).[19]

Turning to R_2NX systems of the sort discussed here, only structural data are available. X-ray crystallography has shown that many nitroxides are bent at N in the solid. The three most bent structures we have seen are related to **4**(O·); **5**,[20] **6**,[21] and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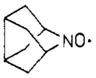
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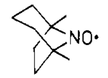
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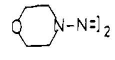
7[22] have α_{av} values of 116.6, 117.5, and 117.4°, respectively. Although nitroxides exist as diamagnetic dipole dimers in the solid state,[23] which could be argued to conceivably have different amounts of bend than the doublet monomeric species do in solution, estimates of the amount of bend from comparison of the observed proton splitting constants for **6** with those calculated for varying degrees of bending agree well with the X-ray structure bend.[21] Because the bending barrier is so low, however, one must be seeing a time-averaged proton splitting over a range of β values and not the average of two rigid structures which were calculated. The problem of matching bend to splittings observed is probably rather complex, but we certainly accept that these nitroxides are, on the average, substantially bent at N in solution, perhaps to the ca. 32% of the way from planar to tetrahedral in terms of α_{av} given by the X-ray structure of **5**.

We believe the small difference in ease of oxidation for **1**(O·) and **2**(O·) provides definite experimental evidence that $\Delta G^{\ddagger}_N$ of **4**(O·) is quite low, probably below 1 kcal/mol, despite the considerable bend at N in this system. This agrees completely with the conclusions of Rassat and co-workers.[9]

Available X-ray structural data for tetraalkyl-2-tetrazenes **8**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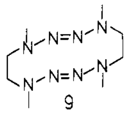
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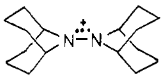
and **9** shows $\alpha_{av} = 113.2$ and 115.5°, respectively,[13] which are quite comparable to the α_{av} values of 113.7 and 115.1–115.5° for substituted morpholine and piperidine cyclohexanone enamines,[24] which have R_2N conjugated with a C=C instead of an N=N bond. They are also approximately the same as for aniline, discussed above. Tetrazene **8** is bent 65% of the way to tetrahedral in terms of its α_{av} value, and **4**(N=]$_2$) is probably at least this bent at N.

Inversion barrier data really do not exist to assess the reasonability of a 5 kcal/mol barrier for 4(N=]$_2$).

$\Delta(\Delta G^{\ddagger}_N)$ and ($\Delta G°_e$) Comparison for Chloramines. A glance at the $\Delta(\Delta G^{\ddagger}_N)$ and $\Delta(\Delta G°_e)$ values for chloramines in parts a and b of Figure 2 reveals the important fact that the $\Delta(\Delta G°_e)$ values are smaller. This is certainly not expected from our previous considerations, because $\Delta(\Delta G°_e) = \Delta(\Delta G^{\ddagger}_N) + \Delta(\Delta G^{*}_e)$, and we know from the nitroxide $\Delta(\Delta G°_e)$ values that $\Delta(\Delta G^{*}_e)$ is positive for **1** and **2**—the $\Delta(\Delta G°_e)$ values "ought to have been" larger than the $\Delta(\Delta G^{\ddagger}_N)$ values, not smaller. The observed values of $\Delta(\Delta G°_e)$ are only about 73 and 77% as large for chloramine **1**(Cl) and **2**(Cl) as Figure 1 predicts by employing the $\Delta(\Delta G^{*}_e)$ values from the nitroxide. We do not believe the effect is caused by experimental errors in $\Delta(\Delta G^{\ddagger}_N)$. Errors could well be introduced by our extrapolating $\Delta G^{\ddagger}_N$ values to 25 °C before plotting them, but even if $\Delta G^{\ddagger}_N$ (T_c) values are used instead, the **1**(Cl) and **2**(Cl) $\Delta(\Delta G^{\ddagger}_N)$ entries are 6.6_7 and 6.1_6, both larger than $\Delta(\Delta G°_e)$ values by far too much for experimental error to account for the anomaly. Because our procedure uses solution data to measure the ease of electron loss and takes differences between different alkyl groups, using the same alkyl groups for both nitroxide and chloramine data, we do not see that invoking solvation changes (which we readily admit are not very well understood) could reasonably account for the anomaly.

In puzzling over how $\Delta(\Delta G°_e)$ could become smaller than $\Delta(\Delta G^{\ddagger}_N)$ for the chloramines, it needs to be pointed out that Figure 3 was constructed by making the assumption that $(R_2NX)^{+\cdot}$ is planar at nitrogen. It is known from X-ray crystallographic structural data that $\mathbf{10}^{+\cdot}PF_4^-$ is planar in the solid,


10$^{+\cdot}$

but it is also known that bending is very easy in tetraalkylhydrazine radical cations, and several examples which are substantially bent at nitrogen are known.[8] σ electron withdrawing groups, especially halogens, are known to favor bending of carbon-centered radicals,[25] and Cl is considerably more σ electron withdrawing than is NR_2. We wish to point out that if $\mathbf{4}(Cl)^{+\cdot}$ were substantially bent at nitrogen, $\Delta(\Delta G°_e)$ would be lowered. If $\mathbf{4}(Cl)^{+\cdot}$ were bent, one would not have to climb all the way to $\Delta G^{\ddagger}_N$ in Figure 3, and $\Delta G°_e$ would be smaller than $\Delta G^{\ddagger}_N + \Delta G^{*}_e$ would predict it to be. R_2N groups **1**–**3** sterically destabilize pyramidal nitrogen atoms significantly more than does **4**. If $\mathbf{4}(Cl)^{+\cdot}$ were bent, $\mathbf{1}(Cl)^{+\cdot}$ and $\mathbf{2}(Cl)^{+\cdot}$ would be less bent and would have to climb closer to $\Delta G^{\ddagger}_N$ in Figure 3 before electron loss occurred. Therefore, if $\mathbf{4}(Cl)^{+\cdot}$ were significantly bent, $\Delta(\Delta G°_e)$ would be lowered and might conceivably be lowered enough to cause $\Delta(\Delta G°_e)$ to be smaller than $\Delta(\Delta G^{\ddagger}_N)$. It is also possible factors not yet considered are responsible for $\Delta(\Delta G°_e)$ being lower than $\Delta(\Delta G^{\ddagger}_N)$ for chloramines.

Irreversible Methylamine Oxidations. Values of $\Delta G^{\ddagger}_N$ could only be measured by ^{13}C NMR for **3**(Me) and **4**(Me). The barrier to nitrogen inversion for **2**(Me) is so low that conformationally caused broadening was not definitely observed down to −150 °C.[2] Because methylamine radical cations deprotonate rapidly, irreversible oxidation peaks were observed by CV. The E_p^{ox} values obtained are not thermodynamically significant numbers because E_p^{ox} is influenced not only by $E°'$ changes but also by the rates of the heterogeneous electron transfer and cation decomposition reactions. It has often been observed, however, that irreversible potentials correlate in a regular way with structural changes.[26] If all of the decomposition reactions were diffusion controlled, only $E°'$ and heterogeneous electron transfer rate constants would affect E_p^{ox}, and depending on how much the electron transfer process changed in rate, E_p^{ox} values changes might reflect principally $E°'$ changes. It is difficult to show for a given set of data what rate and equilibrium constants affect E_p^{ox}, and furthermore E_p^{ox} values are notoriously difficult to reproduce since they usually depend on electrode surface properties. Undaunted, we constructed Figure 2, using E_p^{ox} values in the same way $E°'$ values were used in Figure 1, plotting $\Delta(\Delta E_p) = 23.06\,(E_p^{ox}[\mathbf{4}(Me)] - E_p^{ox}(obsd))$. The pattern generated is in the expected order and the $\Delta(\Delta E_p)$ value for **3**(Me) is between the $\Delta(\Delta G°_e)$ of **3**(Cl) and that of **3**(N=]$_2$), as its $\Delta G^{\ddagger}_N$ value unquestionably is, encouraging us to consider the numbers more closely. We note that $\Delta G^{\ddagger}_N$ for **3**(Me) is 0.4 kcal/mol smaller than $\Delta(\Delta E_p)$. If $\Delta(\Delta E_p)$ really had the same significance as $\Delta(\Delta G°_e)$, we would have expected $\Delta G^{\ddagger}_N$ to be slightly larger, having concluded above that **3** is probably slightly less effective of stabilizing positive change than is **4**. $\Delta(\Delta E_p)$ for **2**(Me) is 3.9_2, and if everything was working,

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this would lead to $\Delta(\Delta G^{\ddagger}{}_{N})$ = 3.4 kcal/mol, because we already decided $\Delta(\Delta G^{*}{}_{e})$ for **2** was about 0.5. This gives $\Delta G^{\ddagger}{}_{N}$ for **2**(Me) of 7.1–3.4 = 3.7 kcal/mol. This number is not unreasonable. Assuming proportionally of $\Delta G^{\ddagger}{}_{N}$ for chloramines and methylamines seems to work as far as it can be tested. For **3**(Me) assuming proportionality gives $\Delta G^{\ddagger}{}_{N}$ = 5.3; the number from NMR measurement is 5.5 kcal/mol. A similar estimate for **2**(Me) is $\Delta G^{\ddagger}{}_{N}$[**2**(Me)] = $\Delta G^{\ddagger}{}_{N}$[**4**(Me)]$\Delta G^{\ddagger}{}_{N}$[**2**(Cl)]/$\Delta G^{\ddagger}{}_{N}$[**4**(Cl)] = 4.1 kcal/mol. Use of the $\Delta(\Delta E_p)$ values as if they were $\Delta(\Delta G^{\circ}{}_{e})$ values does not lead to ridiculous estimates of $\Delta G^{\ddagger}{}_{N}$ values, and $\Delta(\Delta E_p)$ values seem unlikely to be much more than 0.5 kcal/mol away from the $\Delta(\Delta G^{\circ}{}_{e})$ values. Mixing irreversible with reversible oxidation potentials in a single correlation should certainly be avoided, of course.

Nitrogen Inversion Barriers for 1(Cl) and 2(Cl). We have emphasized the assertion that the steric effects of R group size on $\Delta G^{\circ}{}_{e}$ should be mirrored in $\Delta G^{\ddagger}{}_{N}$ and, hence, factored out. It should be pointed out that electronic effects of changing R groups may well also influence $\Delta G^{\ddagger}{}_{N}$. We will not indulge in a general discussion but merely point out a result we did not expect. We found **1**(Cl) to have a 0.5 kcal/mol lower barrier than **2**(Cl)[2] at −95 °C (T_c in both cases), a difference outside of what we believe our experimental error is. This difference also shows up in $\Delta(\Delta G^{\circ}{}_{e})$, a fact of ambiguous significance. Going from 2-methyl-2-azabicyclo[2.2.2]octane [$\Delta G^{\ddagger}{}_{N}$ (−127 °C) = 6.51 (7) kcal/mol] to 1,2-dimethyl-2-azabicyclo[2.2.2]octane [$G^{\ddagger}{}_{N}$ (−127 °C) = 6.68 (8) kcal/mol] increases the barrier slightly,[5] so we had expected **2**(Cl) to have a higher barrier than **1**(Cl). We are unable to quantitatively assess the strain energy differences in either ground or transition state for replacing NCH_3 by NCl. It seems conceivable to us that the origin of the reversal C_1-methylation effect on $\Delta G^{\ddagger}{}_{N}$ in methylamines and chloramines is not steric but electronic. As we have no way of proceeding to a separation of steric and electronic effects here, we must leave the observation as an unexplained one.

Conclusions

For bicyclic R_2NX derivatives **1–4**, when X is Cl, N=]$_2$, or O·, so steric interactions are not increased upon electron removal, $E^{\circ\prime}$ increases in the order **1**(X) < **2**(X) < **3**(X) < **4**(X). The difference in $E^{\circ\prime}$, displayed as $\Delta(\Delta G^{\circ}{}_{e})$ in Figure 1, increases as $\Delta G^{\ddagger}{}_{N}$ increases. These data show that 2-tetrazenes have significantly higher $\Delta G^{\ddagger}{}_{N}$ values than nitroxides. For the methylamines, $E_p{}^{ox}$ changes are in the same order, and $E_p{}^{ox}$ is between $\Delta(\Delta G^{\circ}{}_{e})$ for chloramines and for 2-tetrazenes, as are the $\Delta G^{\ddagger}{}_{N}$ values of methylamines.

Quantitative consideration of the changes in $E^{\circ\prime}$ led to three conclusions. First, $\Delta G^{\ddagger}{}_{N}$ for **4**(O·) and the other nitroxides is very small, in agreement with the conclusions of Rassat and co-workers. Second, $\Delta G^{\ddagger}{}_{N}$ for **4**(N=]$_2$) is estimated to be about 5 kcal/mol. Third, the smaller $\Delta(\Delta G^{\circ}{}_{e})$ than $\Delta(\Delta G^{\ddagger}{}_{N})$ for **1**(Cl) and **2**(Cl) was suggested as being reasonable if **4**(Cl)$^{+\cdot}$ is significantly bent. The latter two conclusions are at present entirely unsupported by any other sort of experimental data. Both are, however, testable in principle. If the **4**(N=]$_2$) $\Delta G^{\ddagger}{}_{N}$ is really 5 kcal/mol, tetrazenes with a more restricted CNC angle will have $\Delta G^{\ddagger}{}_{N}$ in the range measurable by ^{13}C NMR. If **4**(Cl)$^{+\cdot}$ is bent, this might reasonably be expected to affect its spectral properties. Experiments designed to test both of these conclusions are in progress. If it can be established that this procedure has experimental validity, electrochemical measurements can definitely contribute to the understanding of how alkyl group structural changes affect nitrogen inversion rates in conjugated amines, where the barriers are too low to detect by dynamic NMR.

Experimental Section

2-Chloro-1,3,3-trimethyl-2-azabicyclo[2.2.2]octane [**1**(Cl)] was prepared by stirring 1.24 g of amine **9** with 21.7 mL of 5.25% hypochlorite solution (Chlorox) in 13 mL of ether at 0 °C for 1 h, extracting with ether, drying, and concentrating to give **1**(Cl) as an oil. Purification was by Kugelrohr distillation: ^{1}H NMR δ 1.3 (s, 3 H), 1.5 (s), 1.4–2.3 (complex); ^{13}C NMR ($CDCl_3$) δ 64.20 (C_3), 59.61 (C_1), 37.09 (C_4), 30.44 ($C_{6,7}$), 27.92 (C_3CH_3), 27.43 (C_1CH_3), 22.24 ($C_{5,8}$); ^{13}C NMR (1:1 $CD_2Cl_2CF_2Cl_2$) −127 °C δ 65.76 (C_3), 60.96 (C_1), 38.37 (C_4), 36.27 and 27.39 (C_6 and C_7), 28.83 (C_1CH_3), 28.52 (C_3CH_3), 23.48 ($C_{5,8}$); high-resolution mass spectral peak match for $C_{10}H_{18}ClN$.

9-Chloro-9-azabicyclo[3.3.1]nonane [**4**(Cl)] was prepared as previously described:[1] ^{13}C NMR ($CDCl_3$) +54 °C δ 59.96 (C_1), 28.53 (C_2), 19.93 (C_3); ^{13}C NMR ($CDCl_3$) −17 °C δ 59.69 (C_1), 33.58, 23.08 (C_2 and C_6), 20.14 and 19.51 (C_3 and C_7).

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Registry No. 1 (X = Cl), 85029-16-9; **2** (X = O·), 38058-47-8; **2** (X = Me), 85029-17-0; **3** (X = Cl), 5697-97-2; **3** (X = Me), 55100-40-8; **4** (X = Me), 491-25-8; **4** (X = Cl), 73322-95-9.

Chemistry of Oxaziridines. 4.[1] Asymmetric Epoxidation of Unfunctionalized Alkenes Using Chiral 2-Sulfonyloxaziridines: Evidence for a Planar Transition State Geometry

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Abstract: Diastereomeric 2-sulfonyloxaziridines (−)-(*S*,*S*)-**1** and (+)-(*R*,*R*)-**2** epoxidize unfunctionalized olefins **3a–g**, affording epoxides **4a–g** with better enantioselectivity than do chiral peracids or hydroperoxides. The configuration of the oxaziridine three-membered ring controls the stereochemistry of the product. The mechanism of chiral recognition is largely determined by steric factors where the orientations of the oxaziridine three-membered ring and the alkene are planar in the transition state.

The fundamental factors that control asymmetric induction remain unclear despite impressive recent achievements in the asymmetric formation of C–C and C–H bonds.[2,3] This is particularly true for the asymmetric oxidation of unfunctionalized

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