H-14 is corrected to 1.181 ppm in **3**, the resonance would be buried under the strong signal of the methyl H-19 in the "proton-decoupled" spectrum. The other less obvious discrepancy between **1** and **3** occurs at H-8. The difference of 0.12 ppm at a site which is relatively unaffected by substitution may again be due to the uncertainty in the assignment of overlapping peaks in **3**.

These examples illustrate the advantage of the indirect detection by pulse sequence [*A*] which leads to correlation maps and cross sections without any overlap of ^1H peaks. Moreover, in some cases the method can be utilized to ascertain ^{13}C resonances. In **1** and related compounds the assignment of C-15 and C-16 (at approximately 22 and 24 ppm, respectively) is not unanimous,[24a,d,26] but in our study H-15 and H-16 can be distinguished clearly on the basis of NOE difference measurements[22,23] in **2** and **3**. Further confirmation is derived by observing the effect of OAc substitution at position 17 which changes the geminal coupling $^2J_{HH}$ of protons H-15 slightly from 11.8 Hz in **1** to 11.3 Hz in **3**. For protons H-16 the substitution *increases* $^2J_{HH}$ from 13.8 Hz in **1** to 16.1 Hz in **3**. Thus the correlation between the ^1H and ^{13}C chemical shifts facilitates the conclusion that C-15 and C-16 assignment of Highet et al.[24d] is the correct one.

Experimental Section

Progesterone (**1**) was dissolved in $CDCl_3$ to obtain a 0.6 M solution which was put into a 5-mm tube for one-dimensional ^1H and into a 20-mm tube for ^{13}C measurements. The Nicolet NT-300 spectrometer was operating at 300 MHz for protons and at 75.45 MHz for ^{13}C NMR. The routine one-dimensional spectra provided all ^{13}C as well as methyl proton chemical shifts which are reported with respect to internal Me_4Si. Multiplicity of carbon signals was verified by DEPT pulse sequence.[25]

Pulse sequence [*A*] generated 512 blocks each containing 2048 data points with the spectral width ±2976 Hz. The fixed delays were optimized for CH_2 groups (τ = 3.8 ms and τ' = 1.9 ms). The evolution time t_1 was incremented in steps of 1.42 ms. An exponential window function (line broadening 1.0 Hz) apodized ^{13}C signals, and subsequent Fourier transformation separated characteristic resonances along the F_2 dimension. To avoid limitations imposed by a finite size of the computer memory only 8 data points around each ^{13}C signal were transposed. Along the F_1 dimension sinusoidal apodization eliminated broad "tails" around the peaks and zero-filling up to 8192 data points improved digital resolution. The spectra were displayed in the magnitude mode, and their projection onto the F_1 axis was considered as a cross section. This procedure appears more reliable for accurate chemical-shift measurements than the common searching for the maximum signal.

The ^1H chemical shifts were calibrated with respect to the C-18 methyl signal at 0.699 ppm, and the accuracy is approximately 0.005 ppm. The limitations are imposed mostly by inhomogeneity of the external magnetic field, strong coupling, and $^{12}C/^{13}C$ isotope shifts.

Cyclohexanol was studied in a similar way. The only important difference is the fact that traditional cross sections are plotted in a phase-sensitive mode (Figure 2) to show realistic line shapes.

Acknowledgment. The NT-300 spectrometer was purchased partially through a grant from the National Science Foundation (PCM-8115599). This work is partially supported by the National Institute of Health Institutional Biomedical Research Support Grant RR07053.

Registry No. 1, 57-83-0.

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Special Effects of an Unusually Large Neutral to Radical Cation Geometry Change. Adiabatic Ionization Energies and Proton Affinities of Alkylhydrazines

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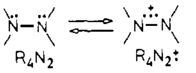
Received January 25, 1984

Abstract: High-pressure mass spectrometry was used to measure adiabatic ionization potentials and proton affinities for hydrazine, methylhydrazine, 1,1-dimethylhydrazine, and six tetraalkylhydrazines. Unusually large relaxation energies in the radical ions, which have vIP − aIP = 1.4–1.6 eV when only H and normal alkyl substituents are present, compared to 0.7 eV for typical amines, reflect the stabilization of the nearly planar hydrazine radical cations by charge delocalization in their three-electron π bonds. The proton affinities of hydrazines are lower than those of comparable amines by 4–6 kcal mol^{-1}. The combined effects of lowered aIPs and lowered PAs decrease the B^+–H bond-dissociation energies in protonated alkylhydrazines by ca. 20 kcal mol^{-1} compared to those of alkylamines.

Previous work on the tetraalkylhydrazine, tetraalkylhydrazine radical cation electron transfer reaction (eq 1) has been recently reviewed.[1] Although R_4N_2 is formally saturated, $R_4N_2^+$ has its positive charge delocalized over both nitrogens and is substantially stabilized compared to radical cations of most saturated compounds. Long lifetimes are observed for $R_4N_2^+$ in solution, allowing measurement of the thermodynamically significant formal potential for electron transfer, $E°'$, for a wide variety of alkyl substituents. Unusual characteristics of this electron transfer include a lack of correlation between vertical ionization potential (vIP) and the electrochemical formal potential $E°'$, a large dependence of the rate of electron loss upon the lone pair–lone pair dihedral angle θ, and very low rates for R_4N_2,$R_4N_2^+$ electron exchange. Those special characteristics result from an unusually



(1)

[†] National Bureau of Standards.

[‡] University of Wisconsin.

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

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large geometry change upon electron loss. Neutral R_4N_2 has approximately tetrahedral nitrogen atoms and an electronic preference for θ of 90°, while $R_4N_2^+$ has a weak preference for planar nitrogens, a strong preference for coplanar lone-pair orbital axes (θ = 0 or 180°), and a far shorter NN bond length than the neutral species.

Because of the stability of $R_4N_2^+$, the adiabatic ionization potentials (aIP) of R_4N_2 should be substantially lower than those of analogous trialkylamines R_3N. However, as a result of the large geometry change, the first ionization peak in the photoelectron spectrum of R_4N_2 is very broad, and reliable adiabatic ionization thresholds cannot be obtained. However, adiabatic ionization values can be obtained from gas-phase charge-transfer equilibria. In these measurements under high-pressure mass-spectrometric conditions, there are long ion residence times in the source ($>10^{-3}$ s) and hundreds of collisions with the carrier gas, C_6H_6, between reactive encounters which allow $R_4N_2^+$ to relax, and therefore the relative energies of the ground-state, geometry-optimized species are obtained.

This work employs high-pressure mass spectrometry to study electron- and proton-transfer reactions for nine hydrazines. In many cases, this technique is not applicable to charge-transfer equilibria since most saturated heteroatom-containing molecules have such rapid radical cation deprotonation reactions that only proton-transfer equilibria are observed. In contrast, most hydrazines exhibit sufficiently slow radical cation deprotonation that electron-transfer equilibration is achieved, allowing direct measurement of adiabatic ionization potential, aIP, differences.

Experimental Section

Measurements were carried out on the NBS pulsed high-pressure mass spectrometer, using the usual procedures.[2] For electron-transfer equilibria 0.01 to 1% solutions of hydrazines in benzene were introduced into a heated bulb and flowed through heated lines to the ion source, where the radical ions of interest were generated by chemical ionization from the benzene radical cation. Methanol was used as a solvent and carrier gas for proton transfer equilibria, and the ions were generated by proton-transfer chemical ionization from $CH_3OH_2^+$ or $(CH_3OH)_2H^+$. Normalized ion intensities of the reference and sample ions were observed for 2–4 ms after the ionization electron pulse.

Alkylated hydrazines were prepared and purified as previously described,[3] and reference compounds were used as purchased (all were of >97% purity).

Results

The adiabatic ionization energies are obtained from charge-transfer equilibria 2 between aromatic reference compounds A of known aIP and the hydrazines of interest B, using eq 3,

$$A^{+\cdot} + B \rightleftharpoons B^{+\cdot} + A \qquad (2)$$

$$\Delta G^\circ = -RT \ln \frac{I_{B^+}}{I_{A^+}} \frac{P_A}{P_B} \qquad (3)$$

where I_{B^+} and I_{A^+} are the ion signal intensities of B^+ and A^+ at equilibrium and P_A and P_B are the pressures of A and B in the ion source.

If equilibrium 2 is to be measured, A^+ and B^+ must be long lived; a possible problem is radical cation deprotonation by neutral B (eq 4) or by neutral reference compound (eq 5). The occurrence

$$B^+ + B \rightarrow BH^+ + (B\text{–}H) \qquad (4)$$

$$B^+ + A \rightarrow AH^+ + (B\text{–}H) \qquad (5)$$

of reaction 4 usually prevents electron-transfer equilibrium measurements involving saturated compounds containing oxygen or nitrogen. The thermochemistry of reaction 4 is given by eq 6, where ΔH°_D is the CH or NH bond-dissociation energy in

$$\Delta H^\circ_4 = \Delta H^\circ_D - \mathrm{PA(B)} - \mathrm{aIP(B)} + \mathrm{IP(H\cdot)} \qquad (6)$$

neutral B. Fortunately, delocalization in $R_4N_2^+$ decreases aIP(B), which can make reaction 4 endothermic for hydrazines. Reaction 4 is not observed for H_2NNH_2 or Me_2NNMe_2, which implies that in these cases reaction 4 is endothermic. This suggests that $\Delta H^\circ_D(H_2NNH\text{–}H)$ is greater than 82 kcal/mol, from eq 6. Although reaction 4 is observed for Me_2NNH_2, it is much slower than exothermic electron transfer to or from the reference compounds used, allowing equilibrium 2 to be measured even though the radical cations are slowly lost by reaction 4. The only system in which proton-transfer reaction 4 interfered with the electron-transfer equilibrium was 2-methyl-1,2-diazabicyclo[2.2.2]octane (**1**). This hydrazine also gives a short-lived radical cation in solution, which was attributed to the fact that its radical cation must have a severely twisted three-electron π bond.[4]

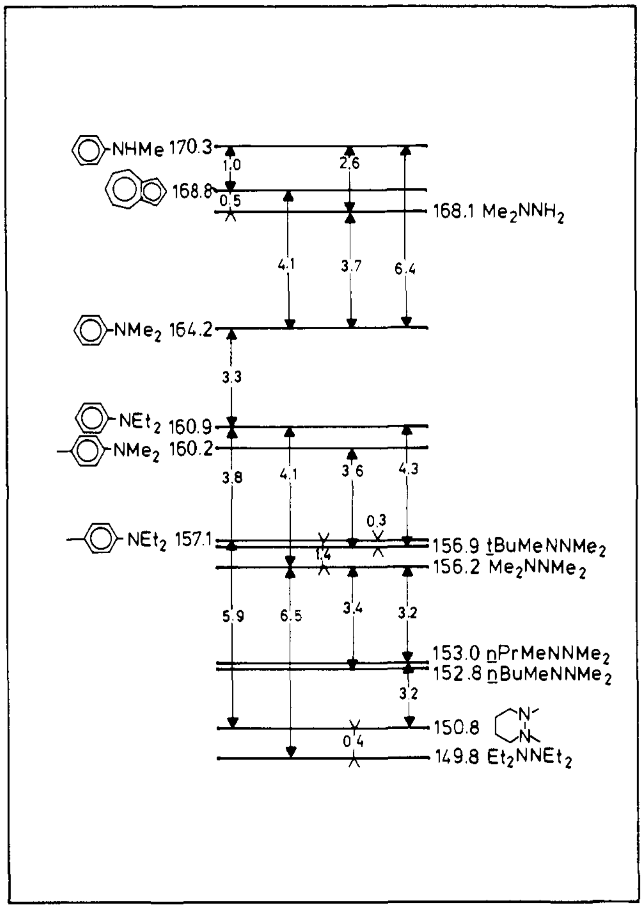
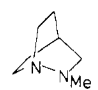


Figure 1. Equilibration ladder for electron transfer between hydrazines and reference compounds at 550 K. Entries are aIP values in kcal/mol. Absolute values are referred to $C_6H_5NMe_2$[6,7] (see text).



1

All equilibrium measurements were repeated two to four times with reaction mixtures where the P_A/P_B ratio was varied by factors of 2 to 10. The equilibrium constants were independent of P_A/P_B, and ΔG° was usually reproducible to ±0.5 kcal/mol (0.02 eV). Because of some of the larger differences between alternative paths in the overlapping scale (see Figure 1), a more conservative error estimate is ±1 kcal/mol (±0.04 eV).

Both H_2NNH_2 and $MeNHNH_2$ were observed to decompose in stainless steel vessels above 200 °C, causing a problem because some of the reference compounds, such as naphthalene, require higher temperatures in the inlet lines. The errors are clearly larger for these compounds. The aIP for H_2NNH_2 reported in Table I is based on equilibrium measurements of $\Delta G^\circ_{480} = +1 \pm 2$

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[2] Meot-Ner (Mautner), M.; Sieck, L. W. *J. Am. Chem. Soc.* **1983**, *105*, 2956.

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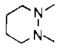
Table I. Comparison of vIP, aIP, and $E^{\circ\prime}$ Values for Alkylhydrazines

compd	vIP,[a] eV	aIP,[b] eV	ΔH_r,[c] eV	$E^{\circ\prime}$,[d] V
H_2NNH_2	9.95	8.1 ± 0.15,[e] 8.36[f]	1.8 ± 0.2	
$MeHNNH_2$	9.35	7.7 ± 0.15,[e] 7.67[f]	1.6 ± 0.2	
Me_2NNH_2	8.85	7.29, 7.46[f]	1.50	
Me_2NNMe_2	8.27	6.78	1.49	0.28
n-$PrMeNNMe_2$	8.14	6.64	1.50	0.27
n-$BuMeNNMe_2$	8.12	6.63	1.49	0.27
t-$BuMeNNMe_2$	7.89	6.79	1.10	0.44
Et_2NNEt_2	7.94	6.50	1.44	0.24
	7.81	6.54	1.27	0.18

[a] Reference 3 and Nelsen et al.: Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 2392. [b] This work. Relative error estimated at ±0.04 eV and absolute error at 0.09 eV, except where noted. Measurements as in Figure 1. [c] ΔH_r = vIP − aIP. [d] Reference 12. CV conditions: acetonitrile containing 0.1 M sodium perchlorate vs. saturated calomel electrode, room temperature. [e] Present work, based on equilibrium measurements as in the text, Results section. [f] Reference 10.

kcal/mol for $H_2NNH_2^+$ + naphthalene → H_2NNH_2 + naphthalene$^+$, aIP(naphthalene) = 188 kcal/mol, and $\Delta G^\circ_{520} = -3 \pm 2$ kcal/mol for $H_2NNH_2^+$ + 1-methylnaphthalene → H_2NNH_2 + 1-methylnaphthalene$^+$, aIP(1-methylnaphthalene) = 183 kcal/mol. The aIP for $MeHNNH_2$ is based on an equilibrium measurement of $\Delta G^\circ_{520} = -0.7 \pm 2$ kcal/mol for $MeHNNH_2^+$ + aniline → $MeHNNH_2$ + aniline$^+$, aIP(aniline) = 178.7.[5-7]

Figure 1 shows the equilibrium ladder for electron transfer between the other hydrazines and reference compounds. The absolute values are referred to aIP($C_6H_5NMe_2$) = 7.12 eV = 164.2 kcal/mol.[6,7]

Our equilibrium results will be seen to require that azulene has a lower aIP than methylaniline. This does not agree with spectroscopic values, where aIP(azulene) is quoted at 171.1 kcal/mol and aIP(methylaniline) at 169.3 kcal/mol.[6,7]

Although the experimental data involve ΔG° measurements, the data are presented in Table I in the conventional form of relative aIP values, using eq 7.

$$\mathrm{aIP(B)} \approx \mathrm{aIP(A)} + \Delta G^\circ{}_1(550) \qquad (7)$$

Equation 7 contains two approximations, eq 8 and 9. Equation 8 assumes negligible entropy effects. However, some entropy

$$\Delta H^\circ{}_1(550) \approx \Delta G^\circ{}_1(550) \qquad (8)$$

$$\Delta \mathrm{aIP} \approx \Delta H^\circ{}_1(550) \qquad (9)$$

changes upon ionization may occur, as the transition from R_4N_2 to $R_4N_2^+$ eliminates the N–N hindered rotor, analogous to the deprotonation of tertiary carbonium ions to olefins, which involves entropy changes of −2 to −4 cal mol^{-1} K^{-1}.[8] For this point to be checked, equilibria 10 and 11 were investigated over a temperature range of 350 and 550 K, giving the enthalpy and entropy change values shown.

$$PhNMe_2^+ + Me_2NNH_2 \rightleftharpoons PhNMe_2 + Me_2NNH_2^+ \qquad (10)$$

$$\Delta H^\circ = 1.0 \pm 1 \text{ kcal mol}^{-1}, \ \Delta S^\circ = -4.8 \pm 2.5 \text{ cal mol}^{-1}\text{ K}^{-1}$$

$$PhNEt_2^+ + Me_2NNMe_2 \rightleftharpoons PhNEt_2 + Me_2NNMe_2^+ \qquad (11)$$

$$\Delta H^\circ = 4.5 \pm 1.5 \text{ kcal mol}^{-1}, \ \Delta S^\circ = -1.2 \pm 3.0 \text{ cal mol}^{-1}\text{ K}^{-1}$$

These results are consistent with the expected sign of the entropy changes. Because of the large error limits in ΔS° and the lack of ΔS° values for the other equilibria, we use "aIP" values calculated by eq 7, recognizing that entropy corrections may render the true aIP values lower by as much as 0.1 eV than those given in Table I. Concerning approximation (9), aIP is defined as $\Delta H_f{}^\circ{}_0(A^+) - \Delta H_f{}^\circ{}_0(A)$, where $\Delta H_f{}^\circ{}_0$ is the heat of formation at 0 K. The difference between ΔaIP and $\Delta H^\circ{}_1(550)$ is given by the differential heat capacity of products and reactants in eq 2, integrated from 0 to 550 K. Using approximation 9 assumes that the *differential* heat capacities are negligible, as has previously been verified for electron-transfer equilibria in aromatic systems.[9]

Considering the experimental error, the reproducibility between replicate measurements, and the uncertainties associated with approximations 8 and 9, the absolute aIP values ought to be accurate to within about ±2 kcal/mol (0.09 V), but as stated above, the relative aIP values should be correct to ±1 kcal/mol (0.04 V).

The proton affinity and protonated hydrazine bond dissociation energy data are given in Table II.

In the following discussion we shall consider the equilibrium values as enthalpy data, bearing the above approximations in mind. Our aIP value for H_2NNH_2 is a little lower than that of Akopian and co-workers,[10] who used high-sensitivity photoionization measurements to estimate aIP, but our substantial experimental error caused by decomposition of the compound makes this conclusion somewhat questionable. Our aIP is significantly lower for Me_2NNH_2. Our aIP value for Me_2NNMe_2 is almost an electron volt lower than the electron impact IP estimated by Dibeler and co-workers,[11] and the "first rise" ionization potential observed in the photoelectron spectrum of Me_2NNMe_2,[12] both of which were 7.76 eV.

Although the present results concern the thermochemistry of the electron transfers, the gas-phase, solvent-free kinetics of charge-transfer reactions are also of interest. While equilibrium is established during the ionizing pulse for reference compound to hydrazine electron transfers, the approach to equilibrium was considerably slower for charge transfers between hydrazines, and equilibrium was only achieved 1–2 ms after the ionizing pulse. Exothermic charge transfer between an alkylhydrazine and a non-hydrazine reference compound appears to occur with near unit efficiency, but the collision efficiency for charge transfer between two alkylhydrazines appears to be in the range 10^{-3}–10^{-4}. This presumably is due to the large geometry charge required for both the neutral and cationic species in these reactions.

Discussion

Relaxation Energies of Trimethylamine and Tetramethylhydrazine Radical Cations. The difference between vIP and aIP is the energy of the relaxation, ΔH_r, for the radical cation going from the geometry of the neutral species to its equilibrium geometry. We will discuss trimethylamine first because its relaxation is simpler than that for hydrazines. Staley and Beauchamp[13] have summarized arguments that the s character of the lone pair increases in the series H_3N, $MeNH_2$, Me_2NH, Me_3N. ΔH_r would be expected to increase because the cations are all planar at nitrogen (p hybridization of the orbital from which the electron was removed). The increase in RNR angle upon ionization will decrease steric interaction between the substituents, tending to decrease ΔH_r in the above series. Although the occurence of reaction 4 has prevented measurement of amine aIP values by direct equilibrium, aIP values derived from photoionization[14] and photoelectron spectroscopy[15] measurements have given good

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(5) The average of values given in ref 6 and 7.

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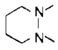
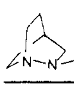
(15) (a) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 311. (b) The range in ΔH_r reported for ten RNH_2 compounds was 0.17 eV, for five R_2NH compounds 0.035 eV, and for five R_3N compounds 0.02 eV. There was no particular correlation of ΔH_r with alkyl group size, except for a lowering of ΔH_r in a di(tertiary alkyl)amine, which was not included in the above range.

Table II. Thermochemistry of the Proton-Transfer Reactions $AH^+ + B \rightarrow BH^+ + A$; Proton Affinities and Homolytic BH^+ Bond-Dissociation Energies of Hydrazines

B	A	$\Delta G°_{600}$[a]	σ_A	σ_{AH^+}	σ_B	σ_{BH^+}	$T\Delta S°_{\sigma}$[a,b]	$\Delta H°$[a,b]	PA(A)[a,c]	PA(B)[a,d]	$PA(B)_{av}$[a]	$\Delta H°_D$-(B^+–H)[a,e]
H_2NNH_2	pyrrole	+4.7	2	1	2	3	−1.1	+3.6	207.6	204.0	204.7[f]	78 ± 3
	cyclopropyl methyl ketone	+0.1	1	1	2	3	−0.4	−0.3	204.0	204.4		
	di-*n*-propyl ether	−2.1	2	1	2	3	−1.1	−3.2	202.3	205.5		
$MeHNNH_2$											214.1[g]	79 ± 3
Me_2HNNH_2	pyridine	+1.3	2	2	1	1	0	+1.3	220.8		219.5[h]	74
Me_2NNMe_2	3-methylpyridine	−2.2	1	1	2	1	0.8	−1.4	224.1	225.8	224.8	67
	2,6-dimethylpyridine	+3.4	1	1	2	1	0.8	+4.2	228.2	224.0		
n-$PrMeNNMe_2$	Me_2NNMe_2	−3.5	2	1	1	1	−0.8	−4.3	224.8	229.1		69
n-$BuMeNNMe_2$	Me_2NNMe_2	−4.4	2	1	1	1	−0.8	−5.2	224.8	230.0		69
t-$BuMeNNMe_2$	2,6-dimethylpyridine	−1.1	2	2	1	1	0	−1.1				72
	N,*N*-diethyl-*p*-toluidine	+1.4	1	1	1	1	0	+1.4				
Et_2NNEt_2	3,6-dimethylpyridine	−3.4	2	2	2	1	0.8	−2.6	228.2	230.8	230.4	67
	N,*N*-diethyl-*p*-toluidine	−1.0	1	1	2	1	0.8	−0.2	229.8	230.0		
	2,6-dimethylpyridine	−1.3	2	2	1	1	0	−1.3	228.2	229.5	229.8	67
	N,*N*-diethyl-*p*-toluidine	−0.2	1	1	1	1	0	−0.2	229.8	230.0		
	Me_2NNMe_2	−4.8	2	1	1	1	−0.8	−5.6	224.8	230.4	230.4	

[a] kcal/mol. [b] $T\Delta S°_{\sigma} = RT \ln (\sigma_{AH^+}\sigma_B/\sigma_{BH^+}\sigma_A)$, $\Delta H°$ calculated from $\Delta H° \simeq \Delta G°_{600} + T\Delta S°_s$. [c] Reference compound proton affinities from the compendium by S. G. Lias to be published in *J. Phys. Chem. Ref. Data*. All proton affinities are referred to $PA(NH_3)$ = 204 kcal/mol. [d] Calculated from PA(B) = PA(A) − $\Delta H°$. [e] Calculated from $\Delta H°_D(BH^+)$ = IP(B) + PA(B) − IP(H·). [f] Compare with the literature value[c] of 206.8 kcal/mol. [g] Aue, D. H.; Bowers, M. J. "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Chapter 9. [h] Compare with the literature value[c] of 220.5 kcal/mol.

agreement. ΔH_r is nearly insensitive to replacement of H by methyl, being 0.69 eV for NH_3 and 0.77–0.78 eV for $MeNH_2$, Me_2NH, and Me_3N.[15b] A reasonable approximation of the energy for flattening at a trialkylamine radical cation is available from the vertical ionization potentials of *n*-Pr_3N (7.92 eV) and 1-azabicyclo[3.3.3]undecane (7.05), for the latter amine is essentially flat at nitrogen, and vIP = aIP.[16] The alkyl groups are about the same size, and the 0.87-eV difference in ionization potentials is rather close to the 0.77 eV reported above for ΔH_r of Me_3N.

Experimentally, ΔH_r is about twice as large for the Me_2NNMe_2 as for Me_3N (Table I). A principal factor increasing ΔH_r for hydrazines is clearly the delocalization available in relaxed $R_4N_2^+$, but there is not a simple relationship between ΔH_r in amines and hydrazines because the relaxation process is more complicated in hydrazines. We compare the ionization behavior of Me_3N and Me_2NNMe_2 in Figure 2, parts a and b. Bent neutral trimethylamine is labelled $B°$, and the planar, relaxed radical cation P^+. vIP is the $B°$,B^+ energy gap, aIP the $B°$,P^+ gap, and ΔH_r the B^+,P^+ gap. We suggest it is also advantageous to consider another pathway from $B°$ to P^+, in which the nitrogen of $B°$ is first flattened to give $P°$, followed by a nearly vertical ionization to P^+. We labeled the $B°$,$P°$ energy gap $\Delta H_N^‡$, because it frequently can be measured by the nitrogen inversion barrier, for which $P°$ is accepted to be the transition state. We used the 7.46-kcal/mol barrier to trimethylamine inversion determined by Koeppl and co-workers[17] from spectroscopic data in constructing Figure 2a. The $P°$,P^+ gap (denoted tIP, ionization from the transition state for nitrogen inversion) cannote be measured experimentally because no $P°$ is present—it is an energy maximum. Nevertheless, because of the geometrical resemblance of P^+ to $P°$, substitution changes which raise the latter should raise the former in energy. Furthermore, we suggest that changes in substituents which affect vIP should affect tIP to a similar degree, because both starting forms have the same attached groups, and both are nearly vertical ionizations. We therefore suggest that consideration of aIP as being composed of $\Delta G_N^‡$ plus tIP will be useful in considering the effect of substituent changes.

The reason for including $\Delta G_N^‡$ and tIP in Figure 2a is to facilitate contrasting ionization processes for amines and hydrazines and emphasize the special effects of hydrazine NN rotation in Figure 2b. Neutral Me_2NNMe_2 has nearly perpendicular lone pairs and bent nitrogens and is labeled *BTB°* (the end letters refer to geometry at nitrogen, *b*ent or *p*lanar, and the middle letter to rotation above the NN bond, *t*wisted or *e*clipsed). The relaxed cation radical has eclipsed alkyl groups and planar nitrogen (*PEP*$^+$). The difference in energy between the vertical cation *BTB*$^+$ and the adiabatic cation *PEP*$^+$ in Figure 2b is not simply related to ΔH_r in Figure 2a, because not only have two nitrogens flattened (vs. only one in Figure 2a), but there has been a 90° rotation about the NN bond, resulting in a large electronic stabilization (formation of the three-electron π bond ($\pi^2\pi^{*1}$) of *PEP*$^+$) and a substantial increase in 1,4 steric interaction of the substituents at nitrogen, which are close to staggered in *BTB*$^+$, but eclipsed in *PEP*$^+$. Bending at nitrogen of hydrazine radical cations (in the *PEP*$^+$ form) is known to be much less costly in energy than bending at the nitrogen of amine radical cations.[1]

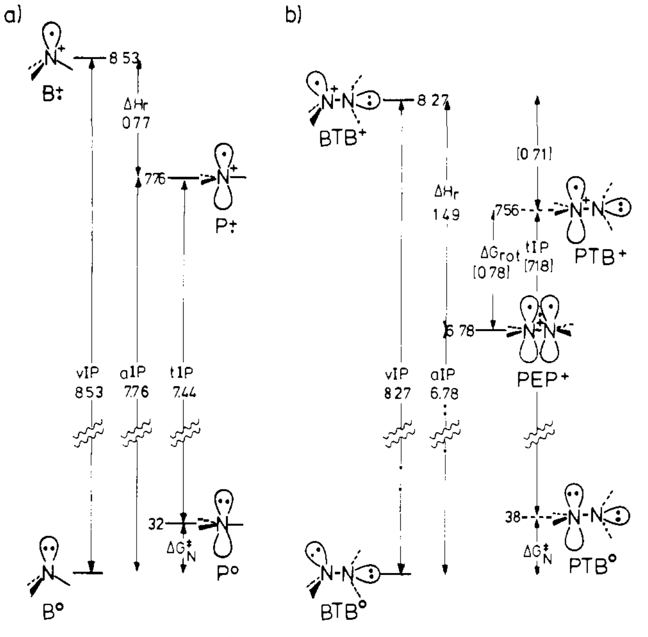


Figure 2. Comparison of ionization energy diagrams for (a) trimethylamine and (b) tetramethylhydrazine.

To probe the relation between ΔH_r and the delocalization energy of the three-electron π bond of *PEP*$^+$, we will consider a nitrogen

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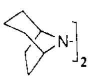
(16) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1975**, *97*, 4136.

(17) Koeppl, G. W.; Sagatys, D. S.; Krishnamurthy, G. S.; Miller, S. I. *J. Am. Chem. Soc.*, **1967**, *89*, 3396.

flattening, ionization pathway analogous to the $\Delta G_N{}^{\ddagger}$, tIP pathway of Figure 2a. The nitrogen inversion barrier in hydrazines is very sensitive to θ,[18] and only one of the nitrogens is planarized at the transition state. Although the single nitrogen inversion barrier for Me_2NNMe_2 has not been experimentally measured, we argue that a reasonable estimate can be made for the difference in this barrier from that of Me_3N by comparing the $\Delta G_N{}^{\ddagger}$ values for amine **2** and hydrazine **1**.[16] The steric environments at the inverting nitrogens of **1** and **2** are similar, and the θ value at the inversion transition state for **1** is held at the most favorable ($\theta = 90°$) value. We therefore estimate the planarization energy at one nitrogen of Me_2NNMe_2 to give the perpendicular ($\theta = 90°$) half-planar species *PTB*° of Figure 2b to be $\Delta G^{\ddagger}(\mathbf{1}) - \Delta G^{\ddagger}(\mathbf{2}) + \Delta G^{\ddagger}(Me_3N)$, the 0.38 eV used in constructing Figure 2b. We estimated the PTB°,PTB$^+$ energy gap (tIP) as being less than IP(Me_3N) by vIP(Me_2NNMe_2) − vIP(Me_3N) = 0.26 eV, using the principle stated above that substituent changes which lower vIP should lower tIP as well. Although Me_3N is not a particularly good model for Me_2NNMe_2, the above estimate gives a relaxation energy for flattening one nitrogen of BTB^+ to give PTB^+ of 0.71 eV, rather close to the analogous energy separation in Me_3N, 0.77 eV. MNDO and ab initio calculations[20] do give the result that the transition state for $H_2NNH_2{}^+$ rotation has perpendicular lone pairs and is most stable in the PTB^+ conformation (one nitrogen planar, one strongly pyramidal), with the charge at nitrogen mostly on the planar nitrogen. The PTB^+,PEP^+ energy difference, labeled $\Delta G^{\ddagger}{}_{rot}$ in Figure 2b, is 0.78 eV. This energy separation corresponds to the NN rotational barrier for PEP^+. The $\Delta G^{\ddagger}{}_{rot}$ for the more highly substituted tetraalkylhydrazine $\mathbf{3}^+$ has recently been measured in acetonitrile,[21] giving 21.8 kcal/mol^{-1} (0.95 V) for the stabler to least stable isomer conversion. This demonstrates that the magnitude of $\Delta G^{\ddagger}{}_{rot}$ in Figure 2b is reasonable, although the difference in both alkyl substitution and phase makes quantitative comparison of these numbers impossible at present. Nevertheless, Figure 2b suggests that flattening at one nitrogen of the vertical $(Me_2NNMe_2)^+$ cation ($BTB^+ \rightarrow PTB^+$) and the NN rotation plus flattening to give relaxed $(Me_2NNMe_2)^+$ ($PTB^+ \rightarrow PEP^+$) are of roughly equal importance in determining ΔH_r.

2



3

Effect of Alkyl Group Change on ΔH_r of Hydrazines. The IP lowering effect of lengthening the chains of alkyl groups (principally a substituent polarizability effect) should affect both vIP and aIP by approximately the same extent. We therefore suggest that their difference, ΔH_r, reflects mainly the difference in alkyl group steric interaction between the equilibrium geometries of the neutral and cationic forms. Because the alkyl groups are eclipsed in PEP^+, introduction of larger groups ought to lower ΔH_r. Lengthening one alkyl chain in the series Me_2NNMe_2, $PrMeNNMe_2$, and n-$BuMeNNMe_2$ gave very similar values of ΔH_r, 1.49–1.50 eV, and that of Et_2NNEt_2 (1.44 eV) is only slightly lower. Booth and Everett[22] recently showed that the change in ring reversal equilibrium for alkylcyclohexanes in solution when an ethyl is substituted for a methyl substitutent is dominated by the $\Delta S°$ term, not the $\Delta H°$ term, as had previously been assumed. To test the relative importance of enthalpy and entropy terms on hydrazine electron transfer equilibria for alkyl group homologation, we investigated reaction 12 between 400 and 550 K, obtaining

$$Me_2NNMe_2{}^+ + n\text{-}PrMeNNMe_2 \rightleftharpoons Me_2NNMe_2 + n\text{-}PrMeNNMe_2{}^+ \quad (12)$$

$\Delta H° = -2.1$ kcal mol^{-1}, $\Delta S° = +1.8$ cal mol^{-1} K^{-1}, so $T\Delta S° = -1.0$ kcal mol^{-1} at 550 K. The $\Delta H°$ term dominated, and enthalpy and entropy effects both favor formation of the larger cation radical, $PrMeNNMe_2{}^+$.

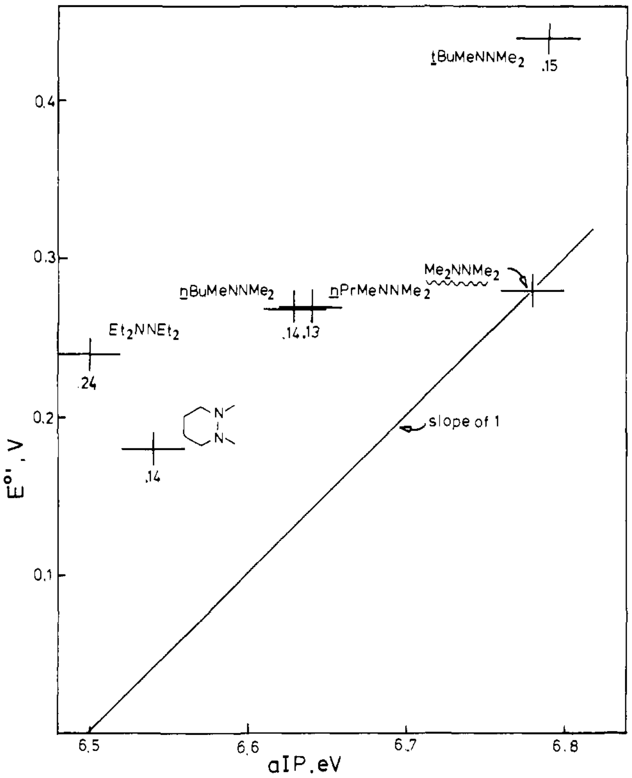


Figure 3. Plot of $E°'$ (V) vs. aIP (eV) for the tetraalkylhdyrazines of Table I.

Introduction of a *tert*-butyl group should sterically destabilize $R_4N_2{}^+$. The ΔH_r of t-$BuMeNNMe_2$, 1.10 eV, suggests that the destabilization relative to Me_2NNMe_2 is large [$\Delta\Delta H_r$ is 0.39 eV (9.0 kcal mol^{-1})]. Inclusion of the hydrazine unit in a six-membered ring should also destabilize the radical cation because of increased eclipsing interactions when atoms of a six-membered ring are flattened.[3] $\Delta\Delta H_r$ for 1,2-dimethylhexahydropyridazine relative to tetramethylhydrazine is 0.22 eV (5.1 kcal/mol). The *tert*-butyl and six-membered ring effects were obvious in the solution phase $E°'$ data,[1,3] but their magnitudes could not be estimated as well because solvation effects could not be separated satisfactorily.

$E°'$, aIP Comparison. Comparison of $E°'$ with vIP revealed the major trends in ΔH_r for tetraalkylhydrazines,[1] but there was no adequate way of separating the effects of solvation from changes in ΔH_r. Knowledge of aIP allows this separation to be made, since changes in $E°'$ are the direct solution analogue of changes in aIP. Changes in $E°'$ are changes in the free energy for electron loss in solution, while the measurements made for aIP are changes in the free energy for electron loss in the gas phase, where solvation effects are absent. Although there could be differences in solvation energy for the neutral hydrazines, we will presume that the major solvation differences involve the much more polar radical cations (at least in non-hydrogen-bonding solvents). If all $R_4N_2/R_4N_2{}^+$ pairs had the same solvation energy as tetramethylhydrazine, a plot of $E°'$ vs. aIP would be a straight line with a slope of one. We show such a plot in Figure 3. In practice, all the points fall above the line. This is reasonable, because the larger alkyl group principally stabilizes $R_4N_2{}^+$ better than a methyl group in the vapor phase because it is more polarizable, and this effect essentially disappears in solution.[23] Another factor may well be

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[18] Nelsen, S. F. *Acc. Chem. Res.* **1978**, *11*, 14.

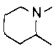
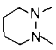
[19] Nelsen, S. F.; Weisman, G. R. *J. Am. Chem. Soc.* **1976**, *98*, 1842.

[20] T. Clark, Universität Erlangen-Nürnberg, private communication. The PTB^+ transition state was found at all levels of ab initio calculation (up to MP2-6-31G*), see ref 21.

[21] Nelsen, S. F.; Cunkle, G. T.; Evans, D. H.; Clark, T. *J. Am. Chem. Soc.* **1983**, *105*, 5928.

[22] Booth, H.; Everett, J. R. *J. Chem. Soc. Perkin Trans. 2* **1980**, 255.

Table III. Comparison of Proton Affinities of Hydrazines and Amines

amine	PA[a]	corresponding hydrazines	PA[a]	ΔPA[a]
$MeNH_2$	214.1	H_2NNH_2	204.7	9.4
MeNHMe	220.6	$MeNHNH_2$	214.1	6.5
Me_2NMe	225.1	$MeNNH_2$	219.5	4.6
Me_2NiPr	229.8	Me_2NNMe_2	224.8	5.0
	~234[b]		229.8	ca 4
	220.8		216.2	4.6

[a] kcal/mol. [b] Estimated from PA(methylpiperidine) + PA(2-methylpyridine – PA(pyridine).

solvent exclusion. Larger alkyl groups are expected to exclude solvent from the region near the nitrogen atoms, the site of formal positive charge. Because the polarizability changes with alkyl group size increase are quite regular, one might hope to be able to separate these two factors with a large series of compounds, but will not attempt to do so with so few examples. We will defer further discussion except to point out that the low slope of the $E^{\circ\prime}$ vs. vIP plot is indeed principally caused by differential solvation.[1]

Proton-Transfer Equilibria. A comparison of amine proton affinities with those of hydrazines which differ from the amines by replacing CH by N is given in Table III. The proton affinities are lower for the hydrazines by 9.4 kcal mol^{-1} for H_2NNH_2, 6.5 kcal/mol for $MeHNNH_2$, and 4–5 kcal/mol for more highly alkylated hydrazines. There is a decrease in proton affinity expected from the electron-withdrawing effect of the second nitrogen, but we cannot separate this from other effects which may be appreciable.[24] We note that the size of the decrease for pyridine vs. 1,2-diazine (last entry in Table III) is about the same as for di- and tetraalkylhydrazines, despite the difference in *n* orbital hybridization.

The far lower bond dissociation energies of protonated hydrazines than protonated amines (difference 33 ± 5 for $MeNH_2$ vs. H_2NNH_2, 20 ± 5 for Me_2NH vs. $MeHNNH_2$, 20 for Me_3N vs. Me_2NNH_2) presumably reflect the combination of inductive effects in the protonated species and resonance stabilization in the radical cations.

Registry No. H_2NNH_2, 302-01-2; $MeHNNH_2$, 60-34-4; Me_2NNH_2, 57-14-7; Me_2NNMe_2, 6415-12-9; *n*-$PrMeNNMe_2$, 60678-65-1; *n*-$BuMeNNMe_2$, 52598-10-4; *t*-$BuMeNNMe_2$, 60678-73-1; Et_2NNEt_2, 4267-00-9; hexahydro-1,2-dimethylpyridazine, 26163-37-1.

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[23] Taft, R. W.; Taagepera, M.; Abbound, J. L. M.; Wol, E. J.; DeFrees, D. J.; Hehre, W. J.; Bartmess, J. E.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 7765.

[24] (a) Bartness, J. E.; Basco, T.; Georgiadis, R. *J. Phys. Chem.* **1983**, *87*, 912. (b) Hinde, R. L.; Pross, A.; Random, L. *J. Comput. Chem.* **1980**, *1*, 118.

Chemical Derivatization of Microelectrode Arrays by Oxidation of Pyrrole and *N*-Methylpyrrole: Fabrication of Molecule-Based Electronic Devices

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Abstract: An array of eight Au microelectrodes, each ~0.12 μm thick, 3 μm wide, and 140 μm long and separated from each other by a distance of 1.4 μm, has been fabricated on a 0.45 μm thick SiO_2 layer grown on a single-crystal Si substrate by use of standard microfabrication techniques. Each electrode can be individually addressed and characterized electrochemically. The individual electrodes can be functionalized with polypyrrole or with poly(*N*-methylpyrrole) by oxidation of pyrrole or *N*-methylpyrrole, respectively, using conditions similar to those for macroscopic electrodes. The amount of polymer deposited can be controlled, and it is possible to electrically "connect" adjacent microelectrodes with deposited polymer. Since the reduced forms of these polymers are insulating and the oxidized forms are electronically conducting, it is possible to prepare electronic devices that are analogous to diodes and transistors using adjacent microelectrodes connected with polymer. The current passing between two microelectrodes connected with polymer as a function of potential between them, and when both are fully oxidized to the conducting state of the polymer, allows a measure of the maximum conductivity of the polymer. We find that polypyrrole is about 10^2–10^3 times less resistive than poly(*N*-methylpyrrole), consistent with previous studies of these two materials. Scanning electron microscopy confirms that polymer can be grown in controlled amounts to selectively connect adjacent microelectrodes.

We wish to report the chemical functionalization of a microelectrode array in a manner that illustrates the fabrication of molecule-based electronic devices having a dimension of 1.4 μm. Our fundamental objective is to illustrate a synthetic methodology that can, in principle, lead to the preparation of aggregate chemical systems that have a specific function. Integration of chemical (and biological) systems with microelectronics seems possible inasmuch as solid-state devices now involve crucial dimensions of the same order as large molecular assemblies. A preliminary communication shows that it is possible to fabricate a molecule-based transistor using three derivatized microelectrodes.[1] This paper is a full account of the procedures used to synthesize such devices.

Our work involves the rational chemical functionalization of an array of small (nominally 2 μm wide × 140 μm long × 0.12 μm thick) Au electrodes. The nominal separation between the 2 × 140 μm Au electrodes is 2 μm. Figure 1 shows a cross-sectional view of the microelectrode array. The particular design is somewhat arbitrary, but the crucial features are that we have

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[1] White, H. S.; Kittlesen, G. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 5375–5377.

0002-7863/84/1506-7389$01.50/0