must be optimized, at least, at the MP2/6-31G level of theory and the zero-point and thermal energy corrections for the neutrals and their corresponding anions must be calculated.[7,13]

At the present level of theory, ab initio is preferable for relative deprotonation energies, and AM1, especially with the corrections suggested, for absolute deprotonation energies.

Acknowledgment. We acknowledge various discussions with Professor J. F. Liebman.

Registry No. **1**, 71-43-2; **1** (anion), 30922-78-2; **2**, 110-86-1; **2** (*o*-anion), 100646-80-8; **3**, 100646-84-2; **4**, 100646-85-3; **5**, 289-80-5; **5** (3-anion), 115590-45-9; **6**, 115561-55-2; **7**, 289-95-2; **7** (2-anion), 115561-56-3; **8**, 115561-57-4; **9**, 115561-58-5; **10**, 290-37-9; **10** (anion), 115561-59-6; **11**, 462-06-6; **11** (*o*-anion), 72863-52-6; **12**, 77748-35-7; **13**, 77748-43-7; **14**, 100-47-0; **14** (*o*-anion), 77748-26-6; **15**, 77748-32-4; **16**, 77748-40-4; **17**, 98-95-3; **17** (*o*-anion), 77748-25-5; **18**, 77748-31-3; **19**, 77748-39-1; **20** (*o*-anion), 115561-60-9; **21**, 100-42-5; **21** (*m*-anion), 115561-61-0; **22**, 78427-92-6; **23**, 115561-62-1; **24**, 98-08-8; **24** (*o*-anion), 77748-27-7; **25**, 77748-33-5; **26**, 77748-41-5; **27**, 83-32-9; **27** (1-anion), 115561-63-2; **28**, 115561-64-3; **29**, 115561-65-4; **30**, 115561-66-5; **31**, 108-88-3; **31** (anion), 18860-15-6; **32**, 108-89-4; **32** (anion), 18860-18-9; **33**, 504-29-0; **33** (anion), 41458-22-4; **34**, 62-53-3; **34** (anion), 27547-14-4; **35**, 536-74-3; **35** (anion), 20404-08-4; $CH_3CONHCH_3$, 79-16-3; CF_3COCH_3, 421-50-1; CH_3COOH, 64-19-7; H_2O, 7732-18-5; CH_3OH, 67-56-1; C_2H_5CN, 107-12-0; 1-methylnaphthalene, 90-12-0; azulene, 275-51-4; pyrrole, 109-97-7; indene, 95-13-6; indole, 120-72-9; naphthalene, 91-20-3; quinoline, 91-22-5.

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[13] Siggel, M. R. F.; Thomas, T. D.; Saethre, L. J. *J. Am. Chem. Soc.* **1988**, *110*, 91.

Proton Affinities and pK_a Values of Tetraalkylhydrazines

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Contribution from the S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, and the Chemical Kinetics Division, Center for Chemical Physics, National Bureau of Standards, Gaithersburg, Maryland 20899. *Received March 14, 1988*

Abstract: Proton affinities for 16 saturated tetraalkylhydrazines were determined by equilibration with triethylamine, 2,6-dimethylpyridine, and 2,6-diethylpyridine using high-pressure mass spectrometry, and pK_a measurements in water were made for the 14 compounds which proved sufficiently soluble. Proton-transfer equilibria for these compounds are compared with electron-transfer equilibria previously measured.

Studies of the effect of changing alkyl groups in tetraalkylhydrazines on equilibrium[1] and rate constants[2] for electron transfer in the gas phase were recently reported, allowing comparison with previous studies in solution. A particularly unexpected result from the comparison of gas- and acetonitrile solution-phase electron-transfer equilibria was that the effect of changing alkyl group size on solvation energy is linear[1b] with the gas-phase "alkyl inductive effect" parameter *n*(eff).[3] *n*(eff) is measured from the ionization potential (IP) lowering effect of larger alkyl groups compared with methyl groups on lone-pair ionizations. It was shown that *n*(eff) can be simply estimated for cyclic and bicyclic alkyl groups and does effectively describe the IP lowering observed when lone-pair rehybridization does not occur. In this work we report equilibrium constant data for gas- and solution-phase proton transfer for a series of tetraalkylhydrazines, allowing comparison of electron loss and proton addition equilibria, both of which generate cations from the neutral compounds.

Results

Gas-phase proton-transfer equilibria for 16 saturated tetraalkylhydrazines were measured at 550 K by high-pressure mass spectrometry by determining their proton-transfer equilibrium constants with monoamines. Triethylamine was used as the primary standard (we took its proton affinity value as PA = 232.3 kcal/mol[4]), and 2,6-dimethylpyridine (A, PA = 228.0) and 2,6-diethylpyridine (B, PA = 230.0) were used as secondary standards, the PA values listed being determined by their equilibration with triethylamine in this work. The $\Delta G°$ (550 K) values measured appear in Table I.

Table I. Proton Affinity Data at 550 K. $\Delta G°$ Values (kcal/mol) for Proton Transfer Relative to Standard Amines

no.	compound	rel to A	rel to B	rel to Et_3N
1	$Me_2N]_2$	+2.8		
2	$EtMeN]_2$	−0.5	+1.4	
3	$nPrMeN]_2$	−2.6		+2.3
4	$nBuMeN]_2$	−3.3		+1.1
5	$nPeMeN]_2$	−3.7		+0.9
6	$iBuMeN]_2$		−2.0	+0.2
7	$neoPeMeN]_2$		−1.4	+0.5
8	$r5N]_2$		−1.8	0.0
9	$r6N]_2$	(−5.1)	−2.2	−0.3
10	$\{5\}Me_2$	+0.2	+2.8	
11	$\{6\}Me_2$	−1.7	+0.4	
12	$\{7\}Me_2$	−1.3	+0.7	
13	$\{5,5\}$	−3.9		+0.7
14	$\{6,6\}$		−1.7	+0.4
15	$\{221\}Me_2$	−3.0		+1.3
16	$\{222\}Me_2$	−4.5		0.0
17	$u\{6\}Me_2$	−1.6		

Symmetrical hydrazines having two formally equivalent nitrogens were studied, including acyclic compounds **1–7** (see the

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† University of Wisconsin.

‡ National Bureau of Standards.

[1] (a) Meot-Ner (Mautner), M.; Nelsen, S. F.; Willi, M. R.; Frigo, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 7384. (b) Nelsen, S. F.; Rumack, D. T.; Meot-Ner (Mautner), M. *Ibid.*, in press.

[2] Nelsen, S. F.; Rumack, D. T.; Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1987**, *109*, 1373.

[3] Nelsen, S. F. *J. Org. Chem.* **1984**, *49*, 1891.

[4] (a) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Chem. Ref. Data* **1984**, *13*, 695. (b) Arnett, E. M.; Jones, F. M.; Taagepera, M.; Henderson, W. G.; Beauchamp, J. L.; Holtz, D.; Taft, R. *J. Am. Chem. Soc.* **1972**, *94*, 4274.

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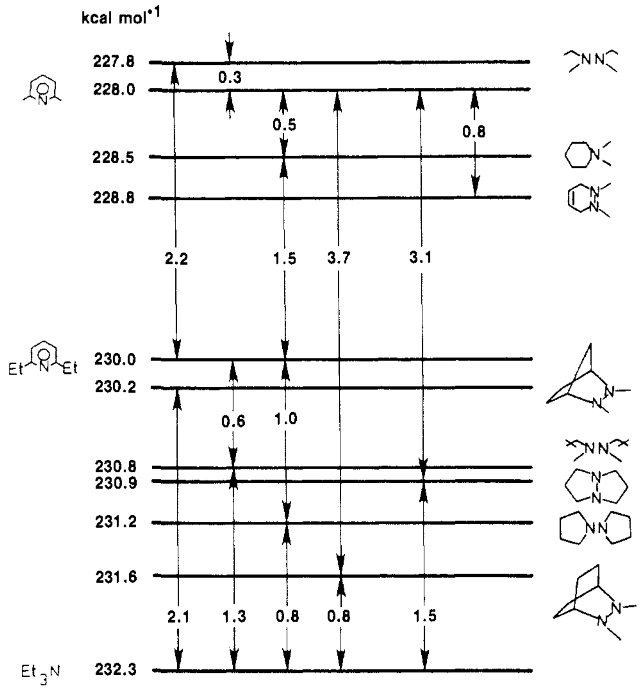
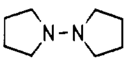


Figure 1. Proton affinity ladder derived from $\Delta G°$ values of Table I.

tables for the structures) and cyclic compounds **8–16**, whose structures are shown below, along with the mnemonic labels used for them in the tables. Data for the unsaturated hydrazine **17** were also taken, and are also included in the tables for completeness, but not in the discussion, because this compound clearly does not follow very closely the trends observed for the compounds with saturated alkyl groups. Even though the olefinic bond is separated from the nitrogens by methylene groups, its influence on formation of cations is substantial. More unsaturated compounds would have to be included in the data set before much interpretation of the values observed could be reliably made.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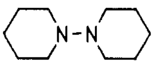
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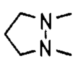
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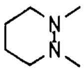
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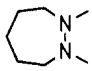
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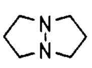
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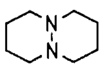
{5,5}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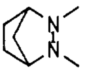
{6,6}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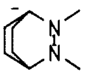
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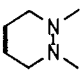
17
u{6}Me$_2$

$\Delta\Delta S°$ values for proton transfer between A and three of the hydrazines {EtMeN]$_2$ (**2**), nPeMeN]$_2$ (**5**), and [r6N]$_2$ (**9**)} were measured as +0.7, 0.0, and 1.1 cal/deg-mol (eu). These values for **2** and **9** are within our experimental error of about 0.5 kcal/mol in $\Delta\Delta G°$ and within the symmetry correction of R ln 2 for having two equivalent nitrogens in the hydrazines but only one in the amine standard. We have used a $T\Delta S°$ correction of +0.8 kcal/mol corresponding to this symmetry correction in converting the $\Delta G°$ values of Table I to the PA values[5] for the hydrazines which are listed in Table II and shown in ladder form in Figures 1 and 2. Compound **5** is somewhat of a special case because of its anomalously low adiabatic ionization potential.[6] It is noteworthy that entropy effects on the proton-transfer equilibria are far smaller than those on electron transfer; the difference in $\Delta S°$ for proton transfer of **2** and **9** was found to be 0.4 eu, while those for electron transfer differed by 5.4 eu (5.8 and 11.2 eu, respectively).[1b] A far smaller geometry change ought to be involved in proton addition, which leaves both nitrogens strongly pyramidal, and electron loss, which causes great flattening at the nitrogen atoms as well as generating a strong preference for coplanar lone-pair orbitals. Also in agreement with a much smaller geometry change for proton transfer than for electron transfer is the fact that the proton-transfer kinetics observed in this work correspond to nearly unit collision efficiency. The only rate constants determined quantitatively were 2.0×10^{-9} cm^3 molecule^{-1} s^{-1} for A, **8** proton-transfer equilibration, and 1.0×10^{-9} for A, **5**, but proton transfer between hydrazines was also observed to be on the order of unit collision efficiency. In contrast, electron transfer between hydrazines, which involves a considerable geometry change, occurs as much as a factor of 10^3 below unit collision efficiency, and the rate constants observed are very sensitive to the structure of the alkyl groups.[2]

Table II. Gas-Phase Proton-Transfer Data for Tetraalkylhydrazines

no.	compound	PA- (550 K) kcal/mol	$\Delta H°$- (N$^+$-H), kcal/mol	δPA, kcal/mol	$\delta\Delta H°$- (N$^+$-H), kcal/mol
1	Me$_2$N]$_2$	224.4	69.2	[0]	[0]
2	EtMeN]$_2$	227.8	69.9	3.4	+0.7
3	nPrMeN]$_2$	229.4	70.8	5.0	+1.6
4	nBuMeN]$_2$	230.4	71.8	6.0	+2.6
5	nPeMeN]$_2$	230.8	69.6	6.4	(+0.4)
6	iBuMeN]$_2$	231.2	72.1	6.8	+2.9
7	neoPeMeN]$_2$	230.8	68.9	6.4	−0.3
8	r5N]$_2$	231.2	64.5	6.8	−4.7
9	r6N]$_2$	231.6	74.1	7.2	+4.9
10	{5}Me$_2$	226.7	66.7	2.3	−2.5
11	{6}Me$_2$	228.9	71.0	4.5	+1.8
12	{7}Me$_2$	228.5	67.6	4.1	−1.6
13	{5,5}	230.9	67.4	6.5	−1.8
14	{6,6}	231.0	72.1	6.6	+2.9
15	{221}Me$_2$	230.2	70.2	5.8	+1.0
16	{222}Me$_2$	231.6	66.7	7.2	−2.5
17	u{6}Me$_2$	228.8	73.6	4.4	4.4

Table III. Comparison of Proton-Transfer Data in Water with Gas-Phase Data for Tetraalkylhydrazines

			$\delta\Delta G°$H^{+a}		
no.	compound	pK_a	H$_2$O	gas	$\Delta G°$s^a
1	Me$_2$N]$_2$	6.18	[0]	[0]	[0]
2	EtMeN]$_2$	6.86	0.9	3.4	2.5
3	nPrMeN]$_2$	7.05	1.2	5.0	3.8
4	nBuMeN]$_2$	7.16	1.3	6.0	4.7
8	r5N]$_2$	7.16	1.3	6.8	5.5
9	r6N]$_2$	7.09	1.2	7.2	6.0
10	{5}Me$_2$	6.67	0.7	2.3	1.6
11	{6}Me$_2$	6.66	0.7	4.5	3.8
12	{7}Me$_2$	6.66	0.7	4.1	3.4
13	{5,5}	7.91	2.4	6.5	4.1
14	{6,6}	6.79	0.8	6.6	5.8
15	{221σbrMe$_2$	6.89	1.0	5.8	4.8
16	{222}Me$_2$	7.14	1.3	7.2	5.9
17	u{6}Me$_2$	5.70	−0.7	4.4	5.1

[a] Units, kcal/mol.

Proton-transfer equilibria in solution for the compounds under discussion were determined by titration in water containing 0.1 M tetraethylammonium perchlorate, making pH measurements using a glass pH electrode. Compounds **5–7** unfortunately proved to be too insoluble in water to allow pK_a measurement; data for the other compounds are included in Table III.

Discussion

1. Gas-Phase Basicity of hydrazines. Both addition of a proton and loss of an electron generate cations from tetraalkylhydrazines.

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(5) Compound **5** shows a lower $\Delta\Delta S°$ value than the symmetry correction would predict, but this might be caused by the large alkyl groups. Aue and Bowers (ref 6, p 15) have attributed the PA anomaly for long-chain aliphatic monoamines to coiling of the chain back to internally solvate the RNH$_3^+$ center, and we noted a similar anomaly, also attributed to internal solvation, for **5** in its gas-phase ET behavior (ref 1b).

(6) (a) Aue, D. H.; Bowers, M. T. *Gas Phase Ion Chemistry*, Bowers, M. T., Ed.; Academic Press: New York, 1979, Vol. 2, Chapter 9. (b) Aue, D. H.; Hebb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 311, 318.

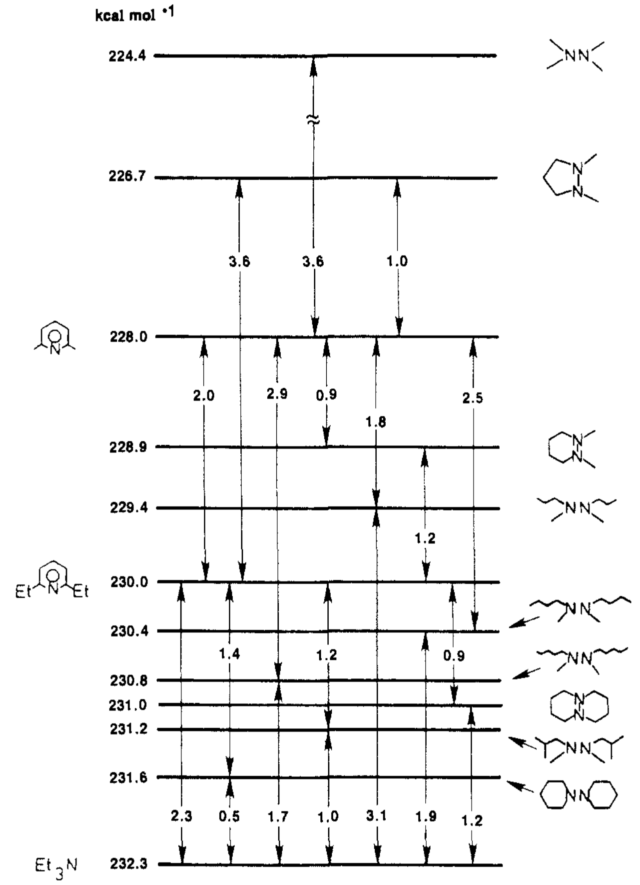


Figure 2. Proton affinity ladder derived from $\Delta G°$ values of Table I.

We shall compare the effects of changing the alkyl group substituents on these equilibria to try to understand more fully their similarities and differences. We restricted this proton-addition equilibrium work to $RR'N]_2$ compounds, the symmetrical substitution pattern being imposed by our inability to distinguish cations protonated at different nitrogens in unsymmetrical compounds because they have the same molecular weight. The cations formed by proton addition and electron loss are both significantly stabilized by enlargement of the alkyl substituents, and the parent tetramethylhydrazine (**1**) is both the least basic (lowest PA) and least easily oxidized (highest vIP) compound studied. The PA for **1** is about 0.7 kcal/mol lower than that for trimethylamine, so the gas-phase basicity of the hydrazine is quite comparable with that of monoamines, which is why it was convenient to measure equilibria relative to monoamines in this work. To facilitate comparison between compounds with different alkyl groups, we plot the increase in proton affinity, δPA = PA(obsd) − PA(1) versus the increase in ease of vertical ionization, δvIP = vIP(1) − vIP(obsd), in Figure 3. If changing the alkyl groups did not lead to significant lone-pair rehybridization in the starting hydrazines and no steric differences were present in the protonated forms, one would anticipate a linear δPA versus δvIP plot, as has been seen by Beauchamp and co-workers for substituted nitriles.[7] This is true within experimental error for the *n*-alkylhydrazines examined, **1–5**, which are shown as the filled circles in Figure 3. The line drawn is a regression through these points, having slope 1.00, intercept 0.10, and an average deviation of 0.28 kcal/mol. We note that lengthening the alkyl groups R in RMeNNMeR causes about the same decrease in vIP as this structural change increases PA. Lengthening the alkyl groups changes two positions β to formally half-positive nitrogens in the cation radical, but at one position β and one position γ to the formally positive nitrogen in the protonated hydrazine. Because there is a rapid falloff of the effectiveness of alkyl group vIP lowering effects (*n*(eff) is 2.0 for Et, 2.48 for nPr, and 2.73 for nBu[3]), this indicates that the effectiveness of alkyl group lengthening at stabilization of the formally positive nitrogen of a protonated hydrazine is approximately twice as great as that at the formally half-positive nitrogen of the vertical cation radical.

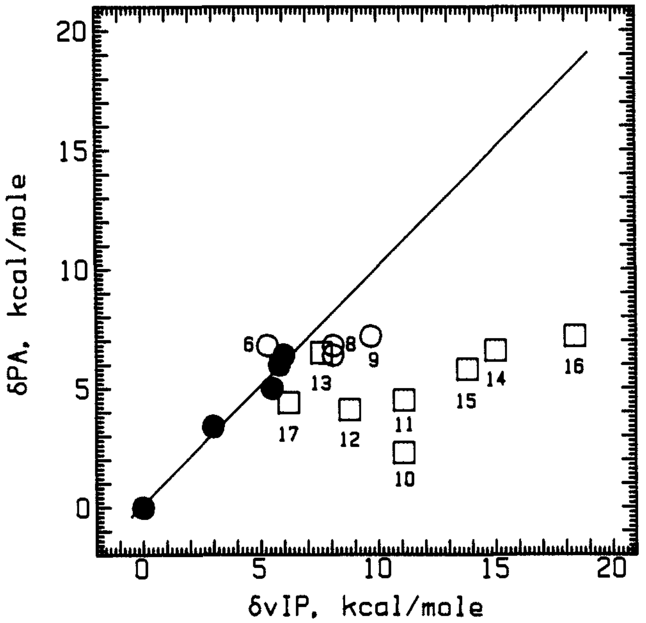
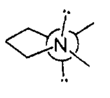
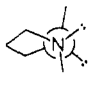


Figure 3. Plot of proton affinity versus vertical ionization potential both shown relative to the values for Me_4N_2 (**1**). The circles show compounds lacking N,N′ rings, all of which have perpendicular lone-pair axes, and the squares show ones with N,N′ rings. The filled circles are the *n*-alkyl cases **1–5**, and the line is the linear regression through these five points only.

The other circles in Figure 3 are for branched alkyl acyclic (**6**, **7**) and *N*,*N*-cycloalkyl (**8**, **9**) compounds which also have near 90° lone-pair, lone-pair dihedral angles, as reflected in similarly small differences between the antisymmetric and symmetric lone-pair combination ionization potentials, $\Delta IP = vIP_1 - vIP_2$ near the 0.51–0.55 eV observed for **1–5**; ΔIP is 0.54 eV for **6**,[8] 0.62 for **7**, 0.56 for **8**, and 0.53 for **9**. The squares are for *N*,*N′*-cycloalkyl compounds **10–17**, many of which show large deviations in the plot. Compounds with large lone-pair, lone-pair interactions (large ΔIP) show large deviations, such as **14** (ΔIP = 2.31 eV), **15** (ΔIP = 1.78 eV), and **16** (ΔIP = 1.82 eV). There is clearly a large decrease in vIP (increase in δvIP) which is not reflected in an increase in PA for such conformations. Several of the compounds studied show two conformations with very different lone-pair splittings in the gas phase, and only the vIP for the major conformation present has been plotted in Figure 3. In each of these cases, the deviation is much larger for the conformation with a larger lone-pair splitting than for that with a smaller one. The major conformations plotted are the Tee conformation of **10** (ΔIP = 2.30 eV) and the ee conformation of **11** (ΔIP = 2.36 eV); the minor conformations Taa-**10** (ΔIP = 0.87) and ae-**11** (ΔIP = 0.74) have δvIP values of −1.4 and 4.4


Tee-10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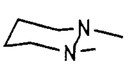
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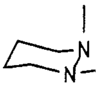
ae-11

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[7] Staley, R. H.; Kleckner, J. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 2081.

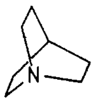
[8] (a) We used the earlier (ref 8b) vIP of 8.03 eV for *N*,*N′*-dineopentyldimethylhydrazine (**7**) in constructing Figure 3, in preference to our more recent measurement[1b] of 8.07 eV. Although these numbers are within the ±0.03 eV quoted overall accuracy for the vIP measurements, we believe the former is to be preferred from examination of Figure 3 (the 8.07 value gives δvIP at 4.4 kcal/mol), as well as from the fact that an anomalously small ΔIP value of 0.48 eV was found in the later work; that in the earlier work was the expected 0.54 eV value. (b) Nelsen S. F.; Peacock, V. E.; Kessel, C. R. *J. Am. Chem. Soc.* **1978**, *100*, 7017.

Scheme I

$$\begin{tikzcd}
B + H^+ \arrow[r, "{[PA(B)]}"] \arrow[d, "{[aIP]}", "-e^-"'] & B^+{-}H \arrow[d, "{[D(N^+{-}H)]}"] \\
B^{+\bullet} + H^+ & B^{+\bullet} + H^\bullet \arrow[l, "{[aIP(H^\bullet)]}"']
\end{tikzcd}$$

kcal/mol, respectively.[1b] **17** shows only the small ΔIP = 0.79 eV gauche lone-pair ae conformation by PE, and is much closer to the *n*-alkyl compound line in Figure 1. We do not believe there is a simple quantitative interpretation to the deviations from the line seen in Figure 3, because the pyramidality at nitrogen changes with ring size and with NN twist angle in the neutral hydrazine, which affects vIP,[7] and conformational changes sometimes will occur upon protonation of one of the nitrogens, which "turns off" the electronic interaction between the lone pairs, but replaces it with a significant anomeric lone-pair, σ^* interaction; the pyramidality at both nitrogens will change between the neutral and protonated forms.

A more quantitative comparison between the proton-addition and electron-loss processes can be made by comparing these equilibria. Scheme I shows the relationship between PA, adiabatic ionization potential aIP, and N^+–H bond strength of the protonated base, $D(N^+{-}H)$; this number is designated $HA(B^{\bullet+})$ by Aue and Bowers.[6] We have used a 313.6-kcal/mol value for $aIP(H^\bullet)$[9]. The aIP measurements have been reported previously.[1b] The N^+–H bond strengths as well as changes in PA and in N^+–H bond strength as the alkyl groups are changed are listed in Table II. The N^+–H bond of a protonated hydrazine is clearly weakened because the hydrazine cation radical produced upon its cleavage has resonance stabilization. Staley and Beauchamp[10] introduced the idea of estimating resonance energy in cations with two amino nitrogens by comparing $D(N^+{-}H)$ for the diamine with that for a model in which the second nitrogen was replaced by a carbon, equating the 14-kcal/mol higher $D(N^+{-}H)$ value for protonated 1,4-diazabicyclo[2.2.2]octane (**18**) than that for protonated 1,4-diazabicyclo[2.2.2]octane (**19**) with the resonance energy of $\mathbf{19}^{\cdot+}$.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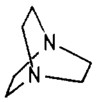
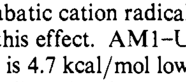

19

Alder, Heilbronner, and co-workers[11] applied this estimate to the higher homologous bridgehead diamines, 1,5-diazabicyclo[3.3.3]undecane and 1,6-diazabicyclo[4.4.4]tetradecane, observing 11 kcal/mol lower $D(N^+{-}H)$ values for the protonated bridgehead diaza compounds than for the monoaza compounds in each case. They pointed out that the strain energies of the protonated diaza and monoaza systems will not in general be the same, and estimated the resonance energy for the diaza cation radicals to be somewhat larger than the difference in $D(N^+{-}H)$ values. We compare $D(N^+{-}H)$ of protonated **1** (69.2 kcal/mol) with that of the parent trialkylamine Me_3N, by combining the aIP value (estimated by Aue and co-workers[12a] at 7.76 eV (179 kcal/mol) from tangential extrapolation of the lone-pair ionization band to locate the first rise point in the PE spectrum of Et_3N[12]), and the proton affinity (estimated at 225.1 kcal/mol[3a]) as indicated in Scheme I, giving $D(N^+{-}H)$ for Me_3NH^+ of 90.4 kcal/mol, a 21.2-kcal/mol higher value than that of protonated **1**. Although objections can be raised for expecting this comparison to truly give the resonance energy of $\mathbf{1}^{\cdot+}$ (isopropyldimethylamine, for which data are not available, would have been a better model, and much larger rehybridizations are occurring at both nitrogens between $\mathbf{1}H^+$ and $\mathbf{1}^{\bullet+}$ than between those of $\mathbf{19}H^+$ and $\mathbf{19}^{\bullet+}$), the number obtained probably is close to the resonance energy of $\mathbf{1}^{\bullet+}$. A completely different method of estimating the resonance energy of a hydrazine cation radical is to measure its rotational barrier, because resonance is completely lost at the transition state for rotation. The free energy barrier separating the stablest, anti form of $\mathbf{20}^{\bullet+}$ from its NN bond rotamer, *syn*-$\mathbf{20}^{\bullet+}$, has been determined[13] in acetonitrile to be 22.0 kcal/mol at 25 °C, and $\Delta H^\ddagger$ to be about 20.2 ± 1.6 kcal/mol.


anti-20

The last column of Table II shows how N^+–H bond strength is affected by replacing the methyl groups of **1** by other alkyl groups. Lengthening *n*-alkyl groups in **1–4** is observed to slightly stabilize the N^+–H bond. Because we believe that these hydrazine cation radicals should all have very close to the same resonance energy and steric interactions between the alkyl substituents on the nitrogens, this only seems reasonable if longer alkyl groups stabilize the protonated hydrazine more than they do the relaxed cation radical. As indicated in Figure 3, stabilization of protonated hydrazines and their vertical cation radicals was found to be about the same in this series. There is also definite experimental evidence that alkyl group homologation is more effective at lowering vIP than it is at lowering aIP. A plot of vIP versus *n*(eff) for **1–5** has a slope 1.6 times that of a plot of aIP versus *n*(eff) for **1–4** (ref 14). Larger lone-pair, N–C(α) combination orbital mixing ought to occur in the much more pyramidal vertical cations than in the nearly planar adiabatic cations, which we suggest is the source of the difference in sensitivity to alkyl group homologation observed for the vertical and adiabatic cation radicals. Semiempirical MO calculations do predict this effect. AM1–UHF calculations[15] give the result that $EtNH_2^{\bullet+}$ is 4.7 kcal/mol lower in heat of formation than $MeNH_2^{\bullet+}$ for the adiabatic, planar (α(av) at N 120°) cation radicals, but the energy difference increases as bending at N is enforced, to 5.0 kcal/mol at $\alpha(av) = 118.7°$ and 5.6 kcal/mol at $\alpha(av) = 110.7°$. A plot of the energy difference versus the change in α(av) from 120° is very nonlinear, with slope decreasing as pyramidality increases in this range. AM1 calculations place $EtNH_3^+$ 8.2 kcal/mol lower in heat of formation than $MeNH_3^+$, which is qualitatively consistent with the larger effect of alkyl group homologation on PA than on vIP found for hydrazines (which shows up as a slope of 1 in the plot of PA versus vIP for RMeNNMeR of Figure 3).

Larger spreads in $\delta DH°(N^+{-}H)$ are observed for the cyclic compounds. Bispyrrolidine (**8**) has the most negative $\Delta DH°(N^+{-}H)$ value observed, while the N,N′ pyrazolidines **10** and **13** also have negative values, as does the N,N′-seven-membered ring compound **12**. In contrast to five- and seven-membered rings causing negative $\delta DH°(N^+{-}H)$ values, that of bispiperidine **9** is the most positive, while those of the N,N^1-six-membered ring compounds **11** and **14** are also both positive. The signs of the deviations for the five- and six-membered ring bicyclic examples **15** and **16** are turned around from those of the monocyclic examples. This pattern is a familiar one to us; the same general pattern as ring size and connectivity are changed is shown by the formal oxidation potentials of these compounds in solution. This point is made in Figure 4, where the relative $E°'(CH_3CN)$ values[8b] for **8–16** are plotted versus $\delta DH°(N^+{-}H)$ values, as the circles. The line shown has a correlation coefficient of 0.98 and an average vertical deviation of 0.5 kcal/mol. Solvation effects are obviously present in the solution phase $E°'$ data. We did not use $E°'$ relative

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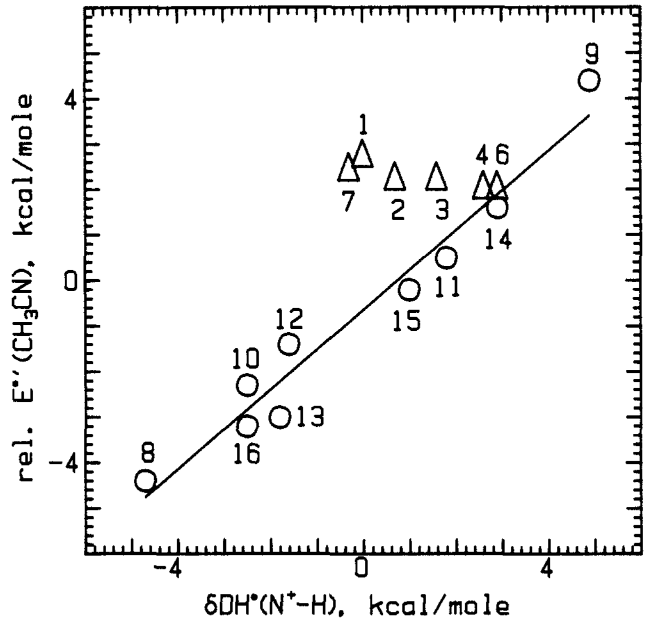

Figure 4. Plot of relative $E^{\circ\prime}$ value in CH_3CN versus N^+–H bond strength in the gas phase. Circles are cyclic compounds, and the line is a linear regression through these data, while the triangles are the acyclic compounds.

to Me_4N_2 for the y axis, but chose an arbitrary value of 0.21 V for the zero of the relative $E^{\circ\prime}$ scale, which makes the x and y axes of Figure 4 cover about the same range. We believe that Figure 4 strongly suggests that the same factor dominates both data sets. We suggest that the relative stability of the hydrazine cation radicals is this dominant factor. The experiments giving rise to the pattern are very different and are even conducted in different phases. The similarity of the pattern of hydrazine cation radical stability produced bolsters our confidence that the relative energies of the hydrazine cation radicals are the principal factor affecting both of these experiments. Aue and co-workers[6b] have previously pointed out the similar size of alkyl group changes on aIP and DH° for amines. Also shown in Figure 4 are the acyclic compounds **1**–**4**, **6**, and **7**, as the triangles. It is noted that the parent compound **1** falls rather far from the line for the cyclic compounds, and the points approach the line as alkyl group size is increased (although the dineopentyl compound **7** falls even farther from the line than does **1**). The changes in alkyl group size are larger for the acyclic compounds (triangles) than for the cyclic ones (circles). For quantitation of alkyl group size effects on solvation energy, see ref 1b.

2. Comparison of Gas- and Solution-Phase Basicity. Table IV contains the pK_a data for **1**–**4** and **8**–**17** in aqueous solution, which is principally of interest here because comparison with the gas-phase data allows calculation of the difference in solvation energy for the proton transfer equilibria. Table III shows differences in free energy for proton transfer at 25 °C in water relative to the equilibrium calculated from eq 1, differences in free energy for

$$\delta\Delta G^\circ H^+(\text{soln}) = 1.36[pK_a(\text{obsd}) - pK_a(1)] \qquad (1)$$

proton transfer in the gas phase calculated from eq 2 (because we believe that the differences in ΔS° are within our experimental

$$\delta\Delta G^\circ H^+(\text{gas}) = PA(\text{obsd}) = PA(1) \qquad (2)$$

error of being zero, we can directly compare the gas-phase data measured at 550 K with room-temperature data in water). The difference between the solution- and gas-phase $\delta\Delta G^\circ H^+$ values represents the effect of free energy of solvation differences for the different compounds on the proton-transfer equilibria, ΔG°s. The values of ΔG°s are strikingly dependent on the size of the alkyl groups attached, and also similar in size to the values observed for electron transfer equilibria in acetonitrile, treated in a similar manner.[1b] However, the large differences in entropy for the electron transfer which are caused by the large geometry change between neutral and cation radical forms of hydrazine necessitated extensive variable-temperature measurements and extrapolation to a common temperature to make the comparison. Figure 5 compares the δG°s values for the proton transfer (the circles) with the electron transfer (the squares) equilibria, plotting each versus n(eff). Because **1** is the reference compound, both sets of data are constrained to have their points for **1** coincide. Quite surprisingly to us initially, the distributions obtained are very similar, and both are within experimental error of being linear with n(eff). The proton-transfer equilibrium regression line has a correlation coefficient of 0.95, an average deviation of 0.47 kcal/mol, and a slope of 1.26, while the electron-transfer equilibrium regression line has a correlation coefficient of 0.94, an average deviation of 0.46 kcal/mol, and a slope of 1.15. A more extensive series of 29 hydrazines was included in the complete data set for the electron-transfer study[1b] without significantly changing the correlation. As pointed out previously, observing linearity with n(eff) shows that exclusion of solvent from the immediate region of the formally positive nitrogen atoms is not a factor, and branching of the alkyl groups or including them in rings does not significantly affect the relative solvation energy observed. What does affect the solvation energy is how good the alkyl groups are at stabilizing the positive charge in the gas phase, which is what the n(eff) values represent. As we pointed out,[1b] this behavior seems most consistent with a picture of the positive charge as being delocalized onto the alkyl groups, which is also the result of MO calculations on the cation radicals. Because water and acetonitrile give such similar plots, it is clear that hydrogen bonding for the neutral tetraalkylhydrazines is not a significant factor. Even the parent tetramethylhydrazine is relatively hindered at the nitrogens, apparently enough that hydrogen bonding is not very important.

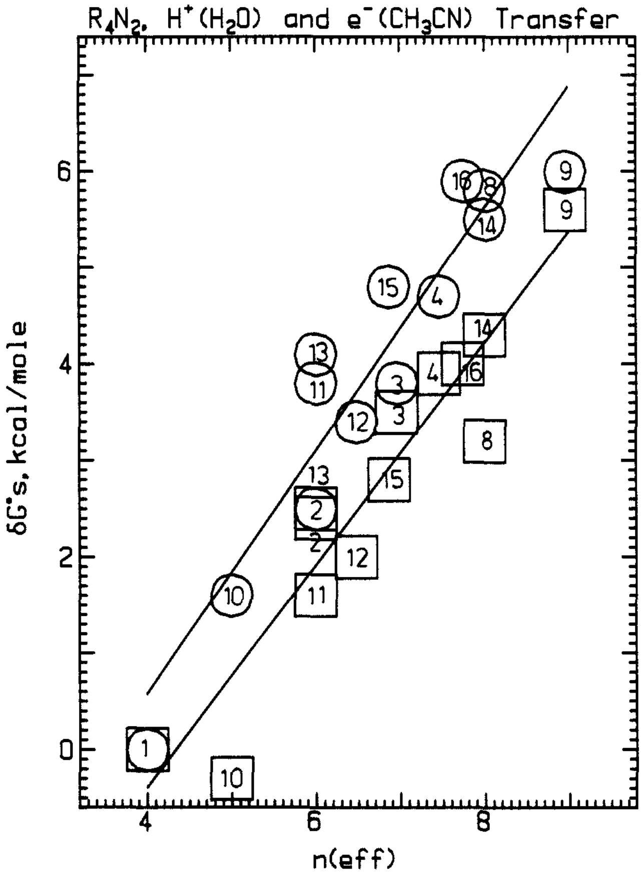

Figure 5. Plots of differences in free energy of solvation for electron-transfer equilibria in acetonitrile solution (squares) and proton-transfer equilibria in water (circles); all data plotted versus n(eff) for the alkyl substituents and shown relative to **1**.

There will surely be some specific solvation of NH^+, but it appears to vary regularly for hydrazines, as pointed out previously for amines by Aue and co-workers.[6b]

Conclusions

Changes in PA as R is homologated in *n*-alkyl RMeNNMeR are approximately the same as changes in vIP. R homologation (mainly from R) stabilizes one NH^+ about the same as two R's stabilize the two half-positive $N^{\bullet +}$ of the cation radical as Aue and co-workers previously showed it does for amines.[6b] Cyclization of the alkyl groups in rings, which changes the lone-pair, lone-pair hybridization and rotational angle, causes much larger effects on vIP than on PA. The changes in gas-phase $D(N^+–H)$ in cyclic hydrazines **8–16** correlate highly with changes in acetonitrile solution $E^{\circ\prime}$ values, suggesting that both are principally determined by changes in hydrazine cation-radical stabilization. Changes in solvation energy as the alkyl groups are changed for both proton transfer in water and for electron transfer in acetonitrile prove to be nearly linear with the gas-phase "alkyl group inductive" parameter *n*(eff). This behavior is not consistent with important specific solvation with the nitrogen lone pairs in the neutral form or with the formally positive nitrogens in the cationic forms for either equilibrium for these rather hindered compounds, even in water. It is also not consistent with the nitrogens actually bearing the positive charge present on the molecules. The positive charge is dispersed onto the alkyl substituents, and approach of solvent near the nitrogens is not required.

Experimental Section

Compound preparation[1b] and the NBS pulsed high-pressure mass spectrometric system[16] have been previously described. Proton-transfer equilibria were studied at 0.1 to 1% hydrazine concentration in methanol as a carrier gas, which produces $CH_3OH_2^+$ as a proton source upon ionization, at 550 K (277 °C). Errors in equilibria measured are estimated to be approximately 0.02 eV (0.5 kcal/mol). Hydrazine pK_a values were measured by titration of 2–4 mM solutions of the hydrazine in dearated, triply distilled water thermostated at 25.0 °C and containing 0.1 M tetraethylammonium perchlorate as supporting electrolyte, using 10% perchloric acid solutions. **10** was studied as the hydrochloride salt, and titrated with 10% NaOH. pK_a values were determined from the inflection point of pH (measured by an Orion Instruments Model 811) versus volume of titrant added plots,[17] and the error is estimated at no more than 0.05 pK unit.

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An ab Initio Investigation of the Stabilization of Selected β-Substituted Ethyl Cations and α-Substituted Methyl Cations

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Abstract: In this study, we calculate the stabilization of β-substituted ethyl cations (R = H, Li, BeH, BH_2, CH_3, NH_2, OH, F, Na, MgH, AlH_2, SiH_3, PH_2, SH, Cl) and α-substituted methyl cations (R = H, Li, CH_3, NH_2, OH, F, Na, SiH_3, PH_2, SH, Cl) in order to obtain a relationship between the nature of the substituent and the degree of stabilization of the cation. Results show that the stabilization energy is related to the electronegativity of the β substituents, but not the α substituents. The rotational barrier of the β-substituted ethyl cation is linearly related to the Mulliken population of the 2p(C+) orbital. We found that the stabilization energy is linearly related to the ionization potential of the α- and PLA β-substituted radicals, and the HOMO energies of the PLA β-substituted radical are linearly related to the corresponding ionization potentials. Trends in the stabilization by second- and third-row substituents are discussed.

A wide variety of theoretical results have been presented which examine substituent effects in carbocation systems.[1-14] Simple theoretical models have been studied as a means of interpreting experimental results obtained for larger, more complex carbocations. As a result, a relatively clear qualitative picture has emerged of the factors that can affect the stability of carbocations.[12]

One way of assessing the stability of a carbocation is to use an isodesmic reaction such as eq 1, where SE+ (SE+ is the

$$RCH_2CH_2^+ + HCH_2CH_3 \xrightarrow{SE+} RCH_2CH_3 + HCH_2CH_2^+ \qquad (1)$$

"stabilization" energy of the cation) is defined as ΔE.[12] (Here we use a β-substituted ethyl cation as an example; an analogous equation would be used for methyl cations.) When SE+ is greater than zero the cation $RCH_2CH_2^+$ is more stable than the corresponding unsubstituted one, $HCH_2CH_2^+$. It has been determined that two distinct types of substituents are capable of stabilizing the cation center. The first consists of substituents more electropositive than H (e.g., BeH, BH_2, AlH_2) that can act as σ-donors and π-acceptors. For the case of carbocations the π-acceptor function is of less importance than for radicals or carbanions.[12]

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* Author to whom correspondence should be addressed.

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