Most of this variation is undoubtedly due to the analytical method but acetophenone gave a lower yield of all hydrocarbons, probably because it reacted photochemically with the product hydrocarbons.

(39) The isotopic purity of $1\text{-}d_6$ must be at least as great as that of the hydrocarbons **3** arising from its decomposition. Of these hydrocarbons, 38% were d_5 and 62% were d_6, giving an isotopic purity of 94%.

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Single-Electron Oxidation Equilibria of Tetraalkylhydrazines. 2. Tetraalkyl-2-tetrazenes as Models for Steric Effects, and the Importance of Alkyl Group Charge Delocalization Anisotropy

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Abstract: Vapor phase vertical ionization potentials (IP_1) were determined by PE spectroscopy for 17 tetraalkyltetrazenes and 14 tetraalkylhydrazines in addition to those previously reported. E^0 vs. SCE values were determined for the tetrazenes and hydrazines in acetonitrile, and for 12 of the tetrazenes, in methylene chloride. From comparisons of these data, it is documented that the charge-stabilizing ability of an asymmetric alkyl group depends on its steric environment, a conclusion supported by MINDO/3 calculations on ethylamine and its cation radical. The 2-tetrazenes are argued to be reasonable steric models for the flattening which occurs at nitrogen upon removal of an electron from a hydrazine. By comparing tetrazene with hydrazine data, it is concluded that the energy for eclipsing the two sets of methyl groups of tetramethylhydrazine in going from the neutral form to the radical cation is about 5 kcal/mol, and that the wide variation in tetraalkyltetrazene E^0 values arises principally because of differences in steric strain between the neutral and radical cation forms.

In a previous paper[1] we reported standard oxidation potentials, $E^{0,2}$ for several tetraalkylhydrazine–tetraalkylhydrazine radical cation ($1,1^+\cdot$) redox couples (see eq 1) as measured by cyclic voltammetry (CV). These E^0 values seem best considered as a series of $\Delta(\Delta G^{\circ})$ values for various $1,1^+\cdot$ equilibria, compared to ΔG° for the parent compound, te-
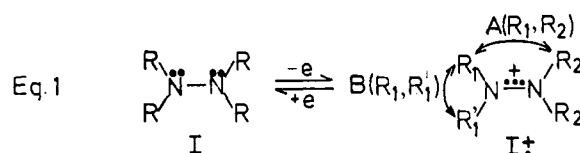
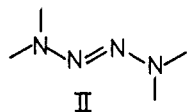**Table I.** Additional Tetraalkylhydrazine Vapor Phase Ionization Potentials and E^0 Values in Acetonitrile Solution[a]

no.	compd	IP_1, eV	$IP_2 - IP_1$, eV	E^0, V vs. SCE
14	n-Bu$_2$NNBu$_2$-n	7.66	0.54	0.24
57	i-BuMeNNMe$_2$	8.07	0.55	0.27
58	i-BuMeNNMeBu-i	8.03	0.54	0.28
21	i-Bu$_2$NNMe$_2$	7.97	0.51	0.29
59	i-Bu$_2$NNMeBu-i	7.90	0.54	0.29
60	i-Bu$_2$NNMBu$_2$-i	7.84	0.53	0.32
61	neo-PeMeNNMe$_2$	8.08	0.58	0.28
62	neo-PeMeNNMePe-neo	7.91	0.62	0.27
63	n-Hept$_2$NNMe$_2$	7.94	0.54	0.25
64	(CH$_2$)$_3$NNMe$_2$	8.28[b]	0.64 (major)	0.24
65	(CH$_2$)$_3$NNPr$_2$-n	8.02[b]	0.65 (major)	0.22
66	(CH$_2$)$_3$NN(CH$_2$)$_3$	8.25[b]	0.73 (major)	0.33
67	(CH$_2$)$_3$NN(CH$_2$)$_5$	7.76[b]	2.04 (major)	0.23
22	(CH$_2$)$_4$NNMe$_2$	8.11[c]	0.60	0.12
25	(CH$_2$)$_4$NN(CH$_2$)$_6$	7.80[d]	0.64	+0.01
29	(CH$_2$)$_6$NNMe$_2$	7.91[d]	0.62	0.18
68	(CH$_2$)$_7$NNMe$_2$	7.87	0.65	0.16

[a] Same conditions as for Table I, ref 1. Numbering is continuous with this paper. [b] From ref 4a. [c] Error found in transcribing numbers in ref 1. [d] Rerun since ref 1; calibration difficulties were later discovered.

Table II. Tetraalkyl-2-tetrazene Vapor Phase Vertical Ionization Potentials and E^0 Values in Acetonitrile Solution

no.	compd	IP_1	$IP_2 - IP_1$, $IP_3 - IP_1$	E^0, V vs. SCE
101	(Me$_2$N=)$_2$	7.71	1.61, 2.09	0.41$_7$[a,b]
102	(EtMeNN=)$_2$	7.51	1.62, 2.10	0.37$_4$[a,b]
103	(n-BuMeNN=)$_2$	7.40	1.66, 2.12	0.36$_1$[a]
104	(Et$_2$NN=)$_2$	7.32	1.63, 2.10	0.32$_7$[a,b]
105	(n-Pr$_2$NN=)$_2$	7.18	1.67, 2.10	0.30$_8$[a,b]
106	(n-Bu$_2$NN=)$_2$	7.12	1.61, 2.09	0.29$_8$[a,b]
107	(i-BuMeNN=)$_2$	7.36	1.64, 2.10	0.36$_1$[a]
108	(i-Bu$_2$NN=)$_2$	7.15	1.64, 2.04	0.31$_7$[a]
109	(neo-PeMeNN=)$_2$	7.27	1.80, 2.12	0.35$_3$[a]
110	(i-PrMeNN=)$_2$	7.36	1.64, 2.10	0.35$_6$[a]
111	(i-Pr$_2$NN=)$_2$	6.91	1.64, 2.18	0.21$_6$[a,b]
112	(t-BuMeNN=)$_2$	7.29	1.48, 2.06	0.21$_3$[a]
113	((CH$_2$)$_3$NN=)$_2$	7.78	1.43, 2.00	0.55[b]
114	((CH$_2$)$_4$NN=)$_2$	7.36	1.74, 2.14	0.31[b]
115	((CH$_2$)$_5$NN=)$_2$	7.52	1.46, 1.97	0.46[b]
116	((CH$_2$)$_6$NN=)$_2$	7.01	1.92, 2.20	0.26[b]
117	((CH$_2$)$_7$NN=)$_2$	6.80	2.10, 2.40	0.18

[a] Determined in a thermostated cell, vs. Ag/Ag$^+$, and believed accurate to ±0.004 V. Reported vs. SCE. [b] Previously reported.[4b] The numbers redetermined (a) are more accurate, but basically agree.

tramethylhydrazine (**1**). ($\Delta(\Delta G^\circ)$, kcal/mol = 23.06 (E^0, $V - 0.28$), because E^0 of **1** is 0.28 V). The principal reason for our interest in this particular redox couple is the great structural change which accompanies electron loss. The flattening at N and twisting and shortening of the N–N bond which accompanies electron loss will increase the R_1R_2 interaction in the cation, causing a positive increment in E^0 (this interaction is symbolized as $A(R_1,R_2)$ in eq 1), and decrease the R_1,R_1' interaction, causing a negative increment in E^0 ($B(R_1,R_1')$ in eq 1). Because **1**$^+$· is electrolytically coupled with **1**, it is easy to obtain thermodynamically significant free energy difference data, and study the effect of changing alkyl substituents upon $\Delta(\Delta G^\circ)$, giving information about bonding and steric interactions in the reactive radical form **1**$^+$· which cannot be easily obtained in other ways.

One factor which must cause E^0 changes for different examples of **1** is the fact that different alkyl groups cause different degrees of stabilization of **1**$^+$· compared to neutral **1**. A way of evaluating the alkyl stabilization effect is to use the vapor phase vertical first ionization potential, IP_1, measured by photoelectron (PE) spectroscopy. Although there is a remarkably general linear correlation between solution oxidation potential and vapor phase ionization potential for a wide range of compound types,[3] a plot of IP_1 vs. E^0 for **1** derivatives showed tremendous scatter (see ref 1, Figure 1). Relative solvation energies for both **1**$^+$· and **1** may be involved in causing the lack of a linear IP_1 vs. E^0 correlation for **1**, but the influence of energies of relaxation corresponding to the decrease in energy between the vertically formed cation which has the bent and twisted geometry of neutral **1** and the relaxed geometry of **1**$^+$· was emphasized.[1]

To identify and help quantitatively evaluate the relative importance of differences in alkyl group charge delocalizing ability, geometric relaxation (A and B effects), and solvation as the methyl groups of **1** are replaced by other alkyl groups, we have carried out PE and CV studies on a series of tetraalkyl-2-tetrazenes, **11**, as well as similar studies on additional examples of **1**. We will establish that the **11,11**$^+$· equilibrium

is an excellent model for **1,1**$^+$· in terms of vapor phase alkyl group delocalization of the positive charge, and argue that a similar flattening at N occurs upon electron loss from **11** as from **1**, making **11** a good model for separating A and B geometry relaxation effects. The A effect is very greatly decreased in **11**$^+$· compared to **1**$^+$·, since the former has an N$_2$ "spacer" between the trisubstituted nitrogens. Quantitative evaluation of the various effects on E^0 for these compounds is attempted and discussed.

Results

The PE IP_1 and CV E^0 values for several hydrazines and tetrazenes are reported in Tables 1 and 11, and additional data appear in ref 1. New compounds are described in the supplementary material. PE data for unsubstituted 2-tetrazene[5a] and some tetraalkyl examples[5b] have been reported in the literature and our data are in basic agreement with the latter. The PE spectra of these tetraalkyltetrazenes show three low-energy maxima which are resolved from the onset of σ ionizations, reasonably assigned in the previous work[5b] as indicating substantial bending from planarity at nitrogen, but large N$_1$ lone pair, N$_2$ π overlap. The similar $IP_1 - IP_2$ and $IP_1 - IP_3$ gaps for the acyclic compounds indicate that little geometry change accompanies alkyl group size change in tetrazenes (as well as in hydrazines), until very large alkyl groups are present (see (t-BuMeNN=)$_2$, **112**, for which some geometry change is evident). In contrast, the 1,1-cycloalkyl compounds **113–117** show somewhat more variation in $IP_1 - IP_2$ and $IP_2 - IP_3$, although we cannot presently interpret the cause for these spectral changes.

Discussion

A. Alkyl Group Charge Delocalization. σ^* **and** μ^*. A widely used quantitation of the charge-stabilizing ability of alkyl groups is given by Taft's σ^* values.[6] Although they traditionally have been called "inductive" parameters, we shall refer to the effect as charge delocalization, since it is well established that larger alkyl groups stabilize not only cationic centers, but also negatively charged species like alkoxides[7] in the vapor phase. Several assumptions are involved in deciding that σ^* values reflect principally charge delocalization effects, and these assumptions have come under heavy criticism, especially by Charton.[8] The criticisms are effectively avoided by the more direct procedure of Danby and co-workers,[9] who defined
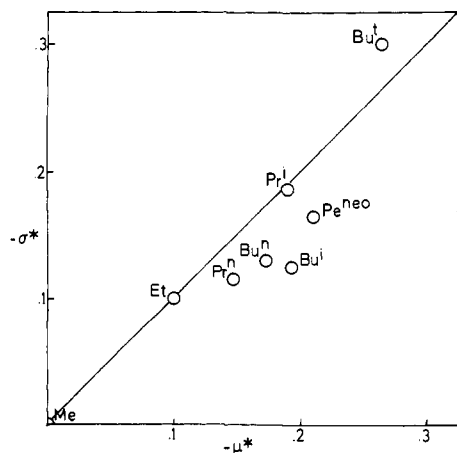
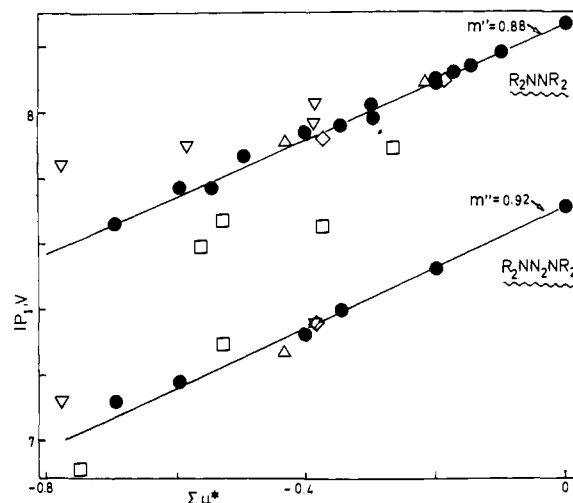**Figure 1.** Plot of $-\sigma^*$ vs. $-\mu^*$ for various alkyl groups.

Figure 2. Plot of IP_1 vs. $\sum\mu^*$ for hydrazines and tetrazenes. The filled circles are for n-alkyl compounds, and the correlation lines drawn consider only these compounds. Other symbols: $\square$, i-Pr$_2$N and t-BuMeN substitution; $\Diamond$, i-PrMeN; $\triangledown$, i-Bu-, $\triangle$, neo-Pe-substituted compounds.

charge delocalization parameters in the vapor phase by using the equation

$$IP_1(RX) = IP_1(MeX) + m'\mu_R \tag{2}$$

averaging the values observed for several lone pair containing X groups.[10] To facilitate comparison with σ^*, we have rescaled μ_R to set the methyl, ethyl gap the same, by taking $\mu^*(R) = 0.512_8\mu_R$. A plot of $-\sigma^*$ vs. $-\mu^*$ appears in Figure 1.[11] Although the charge delocalizing ability of isopropyl is nearly the same by these two very differently derived alkyl group charge delocalization parameters, *tert*-butyl is significantly more negative in σ^* than it is in μ^*. The other significant difference between μ^* and σ^* is the increased effectiveness of alkyl groups containing γ and δ carbons at stabilization of charge in the vapor phase (μ^*) relative to σ^*. The only stabilization possible in the vapor phase is from the alkyl groups attached to the charge-bearing center. Perhaps it is not surprising that the vapor phase measurement, μ^*, "looks farther out" in the alkyl group for stabilization than the solution measurement, σ^*.

Nitrogen-centered systems have more than one site for alkyl group attachment. If only substitution of another alkyl group for methyl is considered, use of the simple additive Danby relationship

$$IP_1 - IP_1^0 = m''\sum\mu^* \tag{3}$$

(IP_1^0 is for the methyl-substituted compound) is justified by the good fit obtained for n-alkylhydrazines I ($m'' = 0.88$, average deviation 11 meV for 14 compounds) and tetrazenes II ($m'' = 0.92$, average deviation 18 mV for 6 compounds), as shown in Figure 2. Although the compounds with longer n-alkyl groups do not deviate from the eq 3 relationship significantly, some of the compounds with branched alkyl groups obviously do (Figure 2). We suggest that two opposing (but interacting) effects are involved. First, when large enough α-branched alkyl groups are present (two isopropyls on one nitrogen and, for I, one *tert*-butyl and one methyl), the observed IP_1 is lower than the n-alkyl correlation line (these compounds are the squares in Figure 2). This would occur if the R_1,R_1' steric interaction was large enough to increase the R_1NR_1' angle, so that the nitrogen lone pair was significantly rehybridized to have more p character than the n-alkyl compounds.[12-15] Higher IP_1 values than the correlation line predicts are obvious for the isobutyl-substituted compounds ($\triangledown$ in Figure 2). Although isobutyl groups are large compared to isopropyl groups (by, for instance, Taft's E_s parameter[6]), they are not α branched and apparently do not result in significant spreading of the R_1NR_1' angle, although the β branching must severely affect the distribution of NCH$_2$R rotational conformers compared to n-alkyl groups. Because charge delo-

calization requires overlap of the alkyl group σ orbitals with the charge-bearing orbital at nitrogen, the effectiveness of overlap and of orbital–orbital interaction is expected to depend on alkyl group conformation. The μ^* values are based on RX compounds in which X is either cylindrically symmetrical or nearly so sterically, such as halides, cyanides, and hydroxides. A restriction in available alkyl group conformations is expected for more hindered compounds such as I and II. We suggest that the distinctly higher IP_1 values than the n-alkyl correlation line for isobutyl-substituted I and II from showing a linear correlation are caused by anisotropy in the charge delocalizing ability of alkyl groups. The principal anisotropy in charge delocalizing ability ought to be involved with the dihedral angle about the :N–CHRR' bond, where rotation causes overlap to be maximized with either C–H or various C–C bonds. To see whether detectable charge delocalization anisotropy is reasonable to postulate, we have carried out MINDO/3 calculations[16] of IP_1 on idealized ethylamine (using bond lengths C–H = 1.47, C–C = 1.54, C–H = 1.09 Å, $\angle$NCC = 109°, and MINDO/3-minimized parameters for $\alpha = 60°$ at the nitrogen atom, N–H = 1.032 Å, $\angle$(HNH) = 104.0°, $\beta = 55.7°$; β is the angle the N–CH$_2$ bond makes with the HNH plane, $\beta = 0°$ for planar N, 54.7° for tetrahedral N) at various $\alpha = $ (CH$_3$CH$_2$–N, lone pair) dihedral angles, while allowing the CH$_2$–CH$_3$ bond to rotate to minimum energy at each α. The results are shown in Figure 3, and give a 0.22-eV change in IP_1 as α is varied, with the maximum IP_1 for gauche α (near 65° is calculated), and minimum for anti α (180°). Isobutyl-substituted I is clearly even more strained in the minimum IP_1 $\alpha = 180°$ conformation than is n-alkyl I, and thus might be predicted to deviate to higher IP_1 in an IP_1 vs. $\sum\mu^*$ plot relative to the n-alkyl correlation line. This is the direction observed. We believe that these ionization potentials establish that μ^* for alkyl iodides is not directly transferable to crowded compounds such as tetraalkylhydrazines and tetrazenes. The deviations observed are admittedly not huge, but are of the approximate magnitude expected from semiempirical calculations.

B. Ring Size Effect on E^0 of II. Significant differences in rate are found for cyclic compared to acyclic examples of a reaction in which a pyramidal atom becomes planar. The five-, seven-, and eight-membered ring examples react faster than acyclic cases, while the six- and four-membered ring examples react more slowly. Brown and co-workers[17] pointed out nearly 30 years ago that differences in eclipsing strain, cross-ring in-
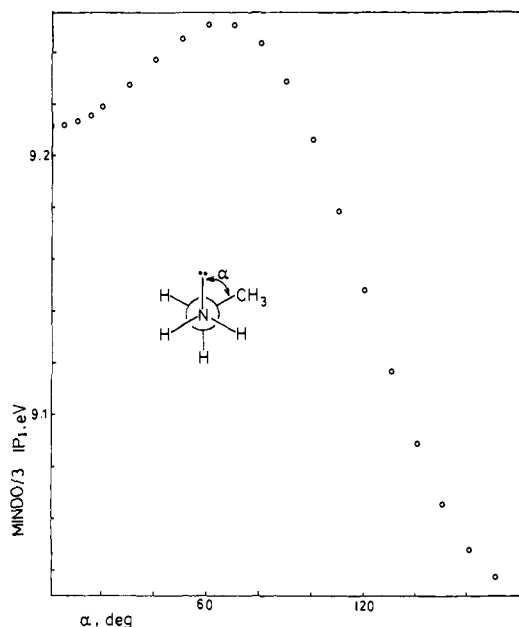
Figure 3. Plot of IP_1 (calculated by MINDO/3) for ethylamine vs. the lone pair N, CH_2CH_3 dihedral angle α.

Table III. $\Delta(\Delta G^{\ddagger})$ Values (kcal/mol) as a Function of Ring Size for Various Reactions[i]

ring size	4	5	6	7	8
Me/Cl, $\xrightarrow{HOAc}$[a]	+0.9	−2.9	0	−2.8	
C=O $\xrightarrow{NaBH_4}$[b]	+0.3	−1.7	0	−2.8	−4.1
CN/N=)$_2$ $\xrightarrow{heat}$[c]	+1.3[d]	−0.9	0	−1.9	−2.5
Me/N=)$_2$ $\xrightarrow{heat}$[c]	+2.4[d]	−0.5	0	−1.8	−2.5
NMe $\xrightarrow{Fe(CN)_6}$[f]		−2.4	0	−3.6	−4.1
NMe E_p^{ox}[g]		−2.8	0	−4.6	−6.1
NN=)$_2$ E^0 values[h]	+0.1[d]	−1.7	0	−2.3	−3.2

[a] Reference 21a. [b] Reference 21c. Observed values multiplied by −1 since the observed reaction takes a trigonal atom to a tetrahedral one. [c] Reference 23. [d] All observed values divided by two since the structural change occurs in two rings at once. [e] Reference 22b. [f] Ref 24a. [g] Reference 24b. [h] This work. [i] The six-ring compound is chosen as the standard for each reaction.

teraction, and angle strain between starting material and transition state all contribute to these rate differences. Rüchardt's group[18] has used the rate–ring size profile to examine the amount of flattening at the transition state for free-radical homolysis reactions,[19] and Lindsay Smith and co-workers[20] have determined such profiles for amine oxidations. In Table III, we give a comparison of the ring size profile of $\Delta(\Delta G^{\circ})$ for biscycloalkyl II with that of $\Delta(\Delta G^{\ddagger})$ for several other reactions, each reaction using the six-membered ring example as the standard compound.[18a] Although different solvents are employed, and the reactions yield cations, radicals, radical cations, or neutral materials as the products, not only is the pattern of signs observed for each case the same, but the magnitudes of the free energy differences are rather similar. We suggest that Table III shows that a similar structural change is occurring at the nitrogen of II during electron transfer as at the analogous positions in the other reactions,
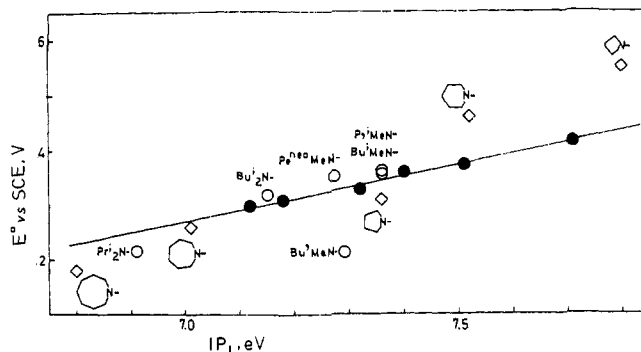

Figure 4. Plot of E^0 vs. IP_1 for tetrazenes. The filled circles are *n*-alkyl examples, and the correlation line only considers these compounds. RRN of the other compounds is given on the plot (points O are branched alkyl, ◊ 1,1-cycloalkyl compounds).

deformation from pyramidal to planar, so that 11 is indeed a viable model for I in terms of geometry change at nitrogen.

Other evidence for pyramidal trisubstituted nitrogens of tetrazenes comes from X-ray crystallographic structural work. The phenyl-*tert*-butyl compound (**118**)[21] has $\beta = 34.1°$. The nitrogens are rather flattened compared to a tetrahedral nitrogen ($\beta = 54.7°$), although the aryl ring is rotated essentially
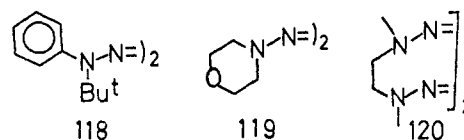
perpendicular to the trisubstituted nitrogen lone pair, so aniline-like resonance is not a factor. For **119**, β is about 44°, and for **120**, 37°.[22] The trisubstituted nitrogens of 11 are only slightly flatter than those of gauche I, where β is 47–51° for the only example yet determined.[23]

C. Steric and Solvation Effects on Tetrazene E^0 Values. Alkyl group charge delocalization differences will clearly affect the E^0 values observed for cyclic as well as acyclic tetrazenes, and we consider separating charge delocalization from steric and solvation effects here. Our plan has been to use IP_1 changes to account for alkyl group charge delocalization (and lone pair rehybridization where the R_1NR' angle is significantly changed), so that deviations from an E^0 vs. IP_1 correlation line would measure the sum of all other effects. A plot of E^0 vs. IP_1 for 11 appears as Figure 4. The six *n*-alkyl examples (filled circles) show, within experimental error, a linear correlation (E^0 (cor) $= -1.17_0 + 0.205_7$ (IP_1), average deviation 4 mV in E^0, maximum deviation 9 mV). The most notable feature of this plot is its low slope. A slope of about 0.9 for E^p vs. IP was observed in the Miller correlation.[3] The structural differences giving rise to the IP_1 changes for 11, alkyl group homologations, are considerably different than the wide range of structural types compared in the Miller correlation. Significant changes in solvent stabilization of the cation as the alkyl groups are homologated probably occur to contribute to the low slope. If solvent stabilization of the radical cation were less effective with longer alkyl groups, as might be expected, this would lower the slope observed. Anisotropy of the charge delocalizing ability of alkyl groups is another possible contributor to the observed low slope. Steric interactions will be significantly different in the geometry of neutral 11 (the geometry for 11[+·] determining IP_1) and in the flattened equilibrium geometry of relaxed 11[+·] (the geometry contributing to E^0). MINDO/3 calculations give the result that the alkyl group conformational effect on the energy of the highest occupied MO of the radical cation is numerically similar to that of the neutral species. Ethylamine radical cation, calculated with planar NH_2 group,
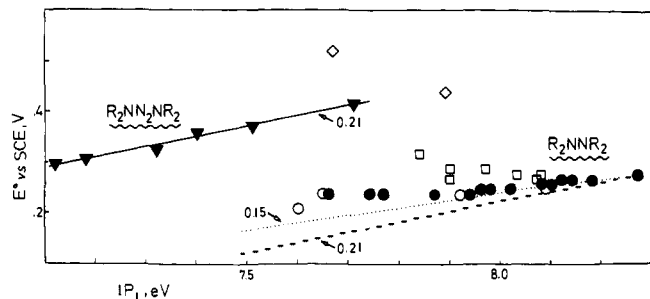
Figure 5. Plot of E^0 vs. IP_1 for acyclic hydrazines (●, *n*-alkyl; ○, *i*-Pr-substituted; □, *i*-Bu and *neo*-Pe-substituted; ◊, *t*-Bu-substituted), compared to *n*-alkyltetrazenes (▼).

Figure 6. Plot of E^0 vs. IP_1 comparing cycloalkyl- and *n*-alkylhydrazines and -tetrazenes. Symbols: ●, *n*-alkylhydrazines; ○, bis-1,1-cycloalkylhydrazines; ◊, 1,1-cycloalkyl-2,2-dimethylhydrazines; ▼, *n*-alkyltetrazenes; ▽, 1,1,4,4-biscycloalkyltetrazenes.

gives the homo at -12.37 eV when the CH_2-CH_3 bond is parallel to the p orbital axis at N ($\alpha = 0°$), and this energy falls to -12.58 eV when $\alpha = 90°$ (the form of the angle dependence is close to but not identical with a $\cos^2 \alpha$ relationship). The difference of 0.25 eV is only slightly higher than the 0.22 eV calculated for the neutral compound. Because the alkyl groups are less congested in relaxed II^+·, a greater fraction of conformations with less effective charge delocalization ought to be available, which would also tend to lower the slope. We have no way of separating these effects (or other possible effects), but note again that the sum of all effects for *n*-alkyl homologation of II results in a linear E^0 vs. IP_1 plot.

Turning to branched alkyl compounds (open circles of Figure 4), both (i-$Pr_2NN=$)$_2$ and (t-$BuMeNN=$)$_2$ show lower E^0 values than the *n*-alkyl correlation line predicts. Strain relief in the flattened radical cation (the $B(R_1,R_1')$ effect mentioned in the introduction) seems a likely rationalization of this fact. The other branched alkyl compounds studied, (i-$PrMeNN=$)$_2$, (i-$BuMeNN=$)$_2$, (i-$Bu_2NN=$)$_2$, and (neo-$PeMeNN=$)$_2$ are expected to have smaller B effects, and are observed to show positive E^0 deviations, corresponding to $+0.2_8$–0.6_2 kcal/mol in $\Delta G°$. We are unable to separate possible differential effects for *n*-alkyl vs. branched alkyl groups on solvent stabilization and alkyl group anisotropy. One way of assessing the relative importance of differential solvent stabilization between *n*-alkyl and branched alkyl compounds is to change solvents, and see if this affects the observed E^0 pattern. No great change in $\delta E^0 = E^0(CH_2Cl_2) - E^0(CH_3CN)$ is observed when *n*-alkyl is replaced by isopropyl or β-branched alkyl groups ($\delta E^0 = +0.09$ to $+0.12$ for **101**–**111**) but a substantial increase in δE^0 to $+0.22$ is observed for (t-$BuMeN-N=$)$_2$, the only tertiary alkyl substituted compound employed. This suggests that a considerably larger differential solvent stabilization effect is occurring for t-Bu-substituted compounds than for the others. Whatever the relative importance of solvation and alkyl group anisotropy actually is, the tetrazene data clearly show a small positive increment in E^0 for β-branched alkyl groups in an E^0 vs. IP_1 plot. Although the $B(R_1,R_1')$ values of i-PrMe and β-branched alkyl compounds are too small to estimate (and we believe that they are likely to be less than experimental error), significantly negative values are observed for B(i-Pr, i-Pr) and B(t-Bu, Me).

For the cycloalkyl compounds (diamonds in Figure 4), we argue that the small size of the branched vs. linear alkyl effect on E^0 encourages just using the vertical deviation from the *n*-alkyl line to give $B(r)$ values, where r is the ring size, as the alkyl groups are unbranched for these compounds. This approximation is clearly worse for the smaller rings than for the large ones. The B values estimated from 2-tetrazene E^0 vs. IP_1 data are $B(4) = +1.3_3$, $B(5) = -0.3_9$, $B(6) = +0.9_6$, $B(7) = -0.1_4$, $B(8) = -0.5_7$ kcal/mol.

D. Steric Effects on Hydrazine E^0 Values. A plot of E^0 vs. IP_1 for acyclic hydrazines is compared with *n*-alkyltetrazene
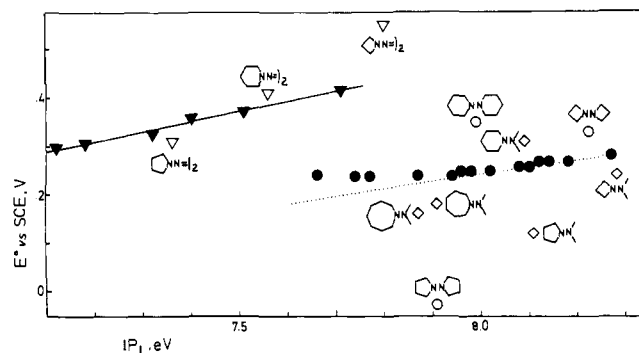
data (triangles) in Figure 5. The most notable feature of this comparison is that, although *n*-alkyltetrazenes have significantly lower ionization potentials than *n*-alkylhydrazines, their E^0 values are distinctly higher, by about 4–5 kcal/mol compared to a hydrazine of the same IP_1. We suggest that solvation is less effective at stabilizing the larger, more dispersed II^+· cation (four-atom π system) than the more localized I^+· cation (two-atom π system).

The *n*-alkylhydrazines (filled circles of Figure 5) show less dependence of E^0 on IP_1 than do the *n*-alkyltetrazenes (triangles), and also exhibit noticeable curvature in the plot. As pointed out in the introduction, eclipsing interactions between the alkyl group on N_1 and N_2 in I^+· (the $A(R_1,R_2)$ effect) will tend to raise E^0 for the larger alkyl-substituted hydrazines. Clear evidence of the importance of the A effect is provided by the *tert*-butyl substituted examples (diamonds in Figure 5), which have far higher E^0 values than the *n*-alkyl compounds. The β-branched alkylhydrazines (squares) also deviate increasingly to higher E^0 as the number of such groups increases. Figure 6 shows an E^0 vs. IP_1 plot in which cycloalkyl compounds are included. Great differences in the E^0 patterns of cycloalkyltetrazenes and hydrazines of similar substitution are observed, despite the similarity of the geometry change at nitrogen. We suggest that these differences are dominated by the $A(R_1,R_2)$ effect, which is essentially lacking for tetrazenes, but important for hydrazines.

To quantitate the A steric effect, we wish to draw lines on Figures 5 and 6, which pass through the standard compound, tetramethylhydrazine, and represent the fall-off in E^0 which would be observed if the $A(R_1,R_2)$ effect were the same size as for tetramethylhydrazine for all the other hydrazines. For the corresponding line of tetrazenes, we could use the line through the *n*-alkyl compounds, since $A(R_1,R_2)$ differences are unimportant because of the nitrogen "spacer" between the trisubstituted nitrogens—we obtained the solid line of slope 0.21 shown in Figures 4–6. Because of the linear E^0 vs. IP relation observed for *n*-alkyltetrazenes, we argue that a linear correlation line from which steric differences should be measurable is reasonable, but the $A(R_1,R_2)$ effect will keep this line from being the best line through the *n*-alkylhydrazines. It also does not follow that the hydrazine slope should be the same as the tetrazene slope (shown as the dashed line of Figure 5), because of the obvious steric and solvation differences for I and II. We have chosen to discuss our data in terms of the equation

$$E^0(cor) = -0.96_1 + 0.15(IP_1) \text{ for } 1 \qquad (4)$$

(the dotted line of Figures 5 and 6) which we will argue gives reasonable $A(R_1,R_2)$ estimates, and we will point out later how the choice of slope affects the numbers derived, and why we

Table IV. A Values (kcal/mol) from Hydrazine E^0 vs. IP_1 Plots, Using Equations 4 and 5

R_1,R_2	$A(R_1,R_2)$	R_1,R_2	$A(R_1,R_2)$
EtMe	$+0.0_7$	5,Me	-1.3_8
nR,Me	$+0.2_2$	6,Me	$+0.1_7$
Et,Et	$+0.1_0$	7,Me	-0.4_6
nR,nR	$+0.3_6$	8,Me	-0.4_1

chose a slope of 0.15 to discuss. Employing eq 4 for E^0(cor), we have used eq 5 to estimate A values. The $B(R,R')$ terms are taken from the tetrazene data.[24]

$$23.06[E^0(\text{obsd}) - E^0(\text{cor})], \text{kcal/mol} = A(R_1,R_2)$$
$$+ A(R_1',R_2') + B(R_1,R_1') + B(R_2,R_2') \quad (5)$$

Application of eq 5 gives the A values which appear in Table IV (average values are used when more than one measure of $A(R_1,R_2)$ is available). We have used the ring size as a symbol for the steric interaction in 1,1-cycloalkyl compounds, defining A similarly to the acyclic compounds (for $(CH_2)_4NNMe_2$, 23.06 $[E^0(\text{obsd}) - E^0(\text{cor})] = 2(A(5,Me) + B(5))$. The effect of changing the slope in eq 4 is basically to increase A when the slope is increased. The change with slope is not large—a 0.09 slope makes $A(n$R,nR$) + 0.1$ kcal/mol, and a 0.21 slope, 0.6_7 kcal/mol. Although the smaller IP_1 of the hydrazine is, the larger the change in the derived A value, using slopes in the range 0.09–0.21 does not change the overall pattern of A values significantly, except to shift all of them relative to zero (which is defined as $A(\text{Me,Me})$). Because of the gauche geometry of the neutral hydrazine and the olefin-like geometry of the radical cation, we believe that the small positive $A(n$R,nR$)$ value we obtain using eq 4 and 5 is quite reasonable. The difference in ΔG^0 for trans to cis isomerization of dialkyl olefins, minus the value for 2-butene, where the substituents are Me,Me, have been most reliably measured by direct equilibration in benzene solution to be nR,Me, $+0.2_3$ and nR,nR, $+0.4_4$ kcal/mol.[25] The cycloalkyl compound A values are interesting in that they suggest an anisotropic methylene–methylene interaction in the radical cation. Both $A(6,6)$ and $A(6,Me)$ are larger than $A(\text{Me,Me}) = 0$, but $A(5,6)$, $A(5,7)$, and $A(6,7)$ are all negative. The larger $A(6,6)$ than $A(5,6)$ and $A(5,7)$ does not depend on the slope chosen in eq 4, but the position of all three relative to $A(\text{Me,Me})$ does. This is not entirely unexpected, and we believe that it is properly rationalized by pointing out that in the relatively rigid chair piperidine ring, the α-equatorial hydrogens are directed toward the alkyl groups on the adjacent nitrogen, while the conformations of five-, seven-, and eight-membered rings are more flexible, and do not require this opposition. The interaction is structurally reminiscent of the $A(1,3)$ interaction in methylenecyclohexanes, the importance of which has been pointed out by Johnson and Malhoutra,[26] and a similar effect is also seen in the relative amounts of gauche and anti conformers of 1,1'-piperidinylazetidine and dipropylaminoazetidine.[4a,27]

$A(5,5)$ is about -2.5 kcal/mol, indicating substantially less alkyl-alkyl steric interaction, relative to $A(\text{Me,Me}) = 0$. Two factors seem to be likely contributors. The methylene groups are held by the rings so their hydrogens are not directed toward the other alkyl group, and the R_1NR_1' angle is restricted by the five-membered ring from enlarging as much as it may in $I^{+\cdot}$. This analysis suggests that the eclipsing interactions in $I^{+\cdot}$ relative to I are at least 5 kcal/mol. Since two eclipsed butane-like interactions are involved, and the N–N bond length decreases markedly on electron removal (over 15% in the one case for which accurate geometrical information is available from X-ray data[28]), this number seems believable to us. The A values obtained from the amino azetidine derivatives are $A(4,Me) = -1.1_4$, $A(4,i\text{-Pr}) = -0.9_3$, $A(4,4) = -0.6_7$. Since

the azetidine alkyl groups are tied back even more than the pyrrolidine alkyl groups, these values are surprisingly positive. We presume that there is some preferential destabilization of the four-membered ring radical cations we have not accounted for (a solvation effect appears likely), and that the A values estimated here are not realistic. We are unable to estimate good A values for the branched alkyl substituents because of the differential solvation and alkyl group charge delocalization anisotropy problems revealed in the 2-tetrazene data (section C).

Conclusion

The charge delocalizing ability of an asymmetric alkyl group is in detail dependent on its steric environment, because it is anisotropic. Although this effect is not very large, it is easily detectable in our data. Thus IP_1 can no longer be accepted to be a perfect measurement of the charge-delocalizing effect of an alkyl group for an E^0 measurement of I and II, because of the conformational difference between the vertical and adiabatic cation. This is clearly a complication in trying to extract the A and B steric effects for hydrazine E^0 values, although the magnitude of the uncertainty thus introduced is not huge. We have attempted to extract as much structural information on hydrazine radical cations as possible by detailed comparison of IP_1 and E^0 values for a long series of hydrazines and tetrazenes. We believe that two major conclusions are independent of our success at dissecting the complex structural effects on steric strain, charge stabilization, and solvation when alkyl group sizes and shapes are altered. First, the vapor phase IP_1 is significantly more sensitive (by a factor of 5 for II, and about 7 for I, independent of the A effect) to alkyl group size than is E^0. Both charge delocalization anisotropy and differential solvent stabilization are probably involved, but measurement of their relative importance has not yet been achieved. Vapor phase measurement of $\Delta(\Delta G^0)$ differences for $1,I^{+\cdot}$ mixtures would give the necessary data for making this separation. Second, the principal factor causing deviations from a linear IP_1 vs. E^0 plot for I and II is the steric strain difference between the neutral and radical cation forms. The lone pair–lone pair dihedral angle θ is not the principal factor of importance in determining E^0, the thermodynamic measure of the ease of electron removal in solution. In contrast, low-temperature CV work on hexahydropyridazine derivatives[29] has shown that θ, and not thermodynamic factors, dominates in determining the rate of electron transfer to an electrode.

Experimental Section

Compound preparation was by established methods, and the details of preparation and spectral properties of the new compounds prepared for this work are summarized in the supplementary material. The PE[30] and CV[1] studies were carried out as previously reported. We are now using the nonaqueous reference electrode, $Ag^0/0.1$ M $AgNO_3$–CH_3CN, which has far better long-term stability and reproducibility in acetonitrile. We observe a $+0.32_4$ V higher E^0 for SCE than $Ag^0/0.1$ M $AgNO_3$–CH_3CN, and all of our data are reported vs. SCE.

Supplementary Material Available: Preparative information for compounds not previously reported, **57–63, 68, 103, 107–109, 112,** and **117;** tabulation of ^{1}H NMR and UV spectra for **101–117,** list of E^0 (CH_2Cl_2) $-$ EP(CH_3CN) for **101–112** (6 pages). Ordering information is given on any current masthead page.

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(24) A drawback to using tetrazene E^0 derivatives to give $B(C_n)$ and applying these directly to hydrazine data, as we have done, arises because of the different pattern of ring size effect on IP_1 for hydrazines and tetrazenes. For the hydrazines both bis-1,1-cycloalkyl and dimethylaminocycloalkyl examples have the six-ring compounds with slightly lower IP_1 than the five-ring compounds (7.91 and 7.89 for N-dimethylaminopyrrolidine and -piperdiene, 8.11 and 8.09 for bispyrrolidine and bispiperidine), but the tetrazene IP_1 values are 7.36 for 114 and 7.52 for 115. Both $IP_2 - IP_1$ values of UV spectra (see the supplementary material) suggest that a conformation charge for 115, bisazopiperidine, relative to the acyclic compounds is principally responsible for the difference in tetrazene IP_1 pattern. If IP_1 of 115 were taken as being $7.52 - 7.36 = 0.16$ eV "too high" because of this conformation change, our analysis would result in $B(6)$ being evaluated at 0.39 kcal/mol too low. We do not think that such an analysis is particularly reasonable, and in spite of the IP_1 anomaly, have used the tetrazene-derived B values throughout our discussion. We do point out that this lengthy footnote is considering a potential 0.4 kcal/mol difference, which is only twice our experimental error, and that solvation differences might well be of this magnitude.

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Transition States for the Hydrolysis of 4-Nitroacetanilide and 4-Nitrothioacetanilide in Varying Concentrations of Sulfuric Acid

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Abstract: The rates of hydrolysis of 4-nitroacetanilide (protonation governed by h_A; $pK_{SH^+} = -2.08$) and 4-nitrothioacetanilide in 22–96% acid, and the activity coefficients of the two compounds in 0–47% acid, have been determined. The change calculated in the activity coefficient (relative to tetraethylammonium ion) of the transition state for the A-2 hydrolysis of 4-nitroacetanilide with changing acid concentration is similar to the change in the activity coefficient of a protonated alcohol, and indicates substantially complete bonding of a water molecule to the protonated amide in the transition state. The same criterion indicates much less complete bonding of a water molecule to the protonated thioamide in the transition state for its hydrolysis.

Introduction

We have recently reported that O-ethyl thiobenzoate hydrolyzes by an $A_{AC}2$ mechanism in all concentrations of aqueous sulfuric acid, while ethyl benzoate hydrolyzes by an $A_{AC}2$ mechanism in acid concentrations up to 80%, but by an

$A_{AC}1$ mechanism in more concentrated acid.[1,2] The change in the activity coefficient of the transition state for the A-2 hydrolysis of ethyl benzoate with changing acid concentration indicates that the transition state has a structure similar to that of a protonated alcohol ROH_2^+, i.e., that the attack of a water