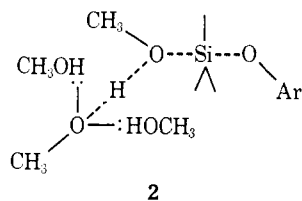of the transition-state protons (fractionation factors $\phi_i{}^T$). The observation of general-base catalysis for the reaction under study[5] suggests a transition state of structure 2. Transition-state contributions to the

2

solvent isotope effect would then come from the bridging proton (fractionation factor ϕ^*) and the two solvent protons in the solvation shell of the catalytic methoxide ion (fractionation factors ϕ_m) so that eq 4 results.

$$k_n(1 - n + 0.74n)^3 =$$
$$k_0(1 - n + n\phi^*)(1 - n + n\phi_m)^2 \quad (4)$$

The latter is easily rearranged to eq 5, of which a plot

$$k_n(1 - n + 0.74n)^3/(1 - n + n\phi_m)^2 =$$
$$k_0(1 - n + n\phi^*) \quad (5)$$

of the left-hand side vs. n should be linear for the correct choice of ϕ_m. Plots are shown in Figure 1 for ϕ_m = 0.8, 1.0, and 1.2. The data are not capable of discriminating strongly among these choices for either substrate. The permitted range of fractionation factors for the bridging proton (determined by the slopes in Figure 1) is ϕ^* = 0.25–0.50, corresponding to k_H/k_D = 2–4. The lower part of this range corresponds to

solvation-bridge effects (2.2 ± 0.7),[9] and the data are therefore consistent with the view that catalysis in these reactions occurs by the one-proton solvation-bridge mechanism. That is, the formation of the silicon-oxygen bond may be assisted by strong hydrogen bonding from the nucleophilic methanol to a catalyzing base. By analogy with other reactions,[9,10] this is probably the most reasonable hypothesis, but the data do not exclude somewhat larger isotope effects for the bridging proton. This could still be consistent with a solvation bridge (which might have a different character and thus a larger isotope effect near a second-row center like silicon), although it might also indicate some participation of the bridging proton in the reaction coordinate.

Experimental Section

Materials. Solutions in CH_3OH and CH_3OD were prepared and manipulated as before.[1,13] p-Chlorophenoxytriphenylsilane was synthesized following a procedure similar to that which Gerrard and Kilburn[14] used to prepare m-trifluoromethylphenoxytriphenylsilane. Recrystallization from diethyl ether gave the silane in 87% yield, mp 96–98°. *Anal.* Calcd for $C_{24}H_{19}SiOCl$: C, 74.50; H, 4.95. Found: C, 74.09; H, 5.09. p-Methoxyphenoxytriphenylsilane was obtained from Schowen.[6]

Kinetic Procedure. Concentrated stock solutions of silanes in dioxane were prepared. Ten microliters of the silane solutions was transferred into the thermostatted cuvet of a Beckman DBG spectrophotometer, and then 2.6 ml of base solutions containing added $LiClO_4$ (0.1500 M) was injected rapidly. Wavelengths used for following the kinetic progress of reaction were 284 nm for p-chlorophenoxytriphenylsilane and 290 nm for p-methoxyphenoxytriphenylsilane.

(14) W. Gerrard and K. D. Kilburn, *J. Chem. Soc.*, 1536 (1956).

Photoelectron Spectra of Hydrazines. IV. Empirical Estimation of Lone Pair-Lone Pair Dihedral Angles and Prediction of Lone Pair Ionization Potentials for Some Cyclic and Bicyclic Hydrazines

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Abstract: The curve calculated for the difference in lone pair ionization potentials (Δ) as a function of the lone pair–lone pair dihedral angle (θ) using INDO calculations on idealized tetramethylhydrazine is presented, and scaling to give more realistic θ angles from experimental spectra is discussed. The changes in $\Delta(\theta)$ expected for flattening of the nitrogens from tetrahedral geometry have been calculated. The spectra of five cyclic dialkylhydrazines are given, from which empirical parameters are derived which are used to calculate the average ionization potentials for 12 cyclic tetraalkylhydrazines. These calculations were fairly successful for cyclic hydrazines, showing Δ values less than 1 eV, but not satisfactory for tetraalkylhydrazines having large Δ values.

Rademacher[1] and we[2] have noted that, since the amount of interaction between the lone pair electrons of a hydrazine should be dependent upon the dihedral angle θ between the lone pair orbital axes,

photoelectron spectroscopy (pes) should be of use in determination of hydrazine conformations. As Hoffmann[3] has pointed out, the lone pair orbitals will interact to form two molecular orbitals, of which the symmetric lone pair combination (n_+) will be bonding and hence lower in energy (higher in ionization poten-

(1) (a) P. Rademacher, *Angew. Chem.*, **85**, 410 (1973); (b) P. Rademacher, *Tetrahedron Lett.*, 83 (1974).
(2) (a) S. F. Nelsen and J. M. Buschek, *J. Amer. Chem. Soc.*, **95**, 2011 (1973); (b) *ibid.*, **95**, 2013 (1973); (c) *ibid.*, **96**, 2392 (1974).
(3) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

n_+ n_-

tial) at θ values below about 90°, whereas the antisymmetric (n_-) combination will be lowest in energy at high θ values. The lone pair ionizations of saturated aliphatic hydrazines are usually well separated from σ-bond ionizations, allowing measurement of their positions. We choose to express these ionizations in terms of their average, $IP_{av} = (IP_1 + IP_2)/2$, and their separation, $\Delta = IP_2 - IP_1$, where IP_1 is the lowest ionization potential.

For the series of the five methylated hydrazines, we found that calculated orbital energies (INDO approximation, using idealized geometries and $\theta = 90°$ for all five compounds), E_i, when plotted against the ionization potentials gave a good straight line having a standard deviation of 42 meV for the ten points.[2c] Since our experimental error is (conservatively) 30 meV, it appears that the INDO calculations adequately correlate both Δ and IP_{av}, suggesting that the methylated hydrazines have roughly similar θ values.

Calculations on hydrazine and tetramethylhydrazine in which θ was varied from 0 to 180°, invoking Koopman's theorem to equate $-E$ with IP, give the prediction that Δ follows a rough $\cos \theta$ relationship, although the magnitudes of $\Delta(0°)$ and $\Delta(180°)$ were different, and the "crossover points" (where n_+ and n_- have the same energy, $\Delta = 0$) were slightly different (83° for tetramethylhydrazine, 85.5° for hydrazine), and the tetramethylhydrazine curve was rather flatter than that of hydrazine near 180°. This suggests that a $\Delta(\theta)$ function, to be used as a working curve for evaluation of θ from experimental Δ values, ought to take into account the substitution pattern of the hydrazine; hydrazine itself is expected to show a larger Δ value for a given θ value than is tetramethylhydrazine (except very near the crossover point).

Since it is impractical to perform MO calculations on all molecules for which we would like to interpret pes spectra, we have made the assumption that substitution of one alkyl group for another (if θ does not change) is a small effect which will show up principally in IP_{av}, leaving Δ unchanged. The independence of Δ with substituent changes was borne out experimentally, since nine tetraalkylhydrazines with Me, Et, i-Pr, n-Pr, n-Bu, and t-Bu substituents showed quite constant Δ values[2c] (eight in the range 0.51–0.55 eV, and only the most hindered one, triisopropylmethylhydrazine, having a slightly larger splitting of 0.61 eV). The IP_{av} values ranged from 8.55 to 7.90 for this series. A quantitative method of accounting for the IP_{av} values was devised, defining a parameter, $X(R)$ (eq 1), obtained from monoalkylhydrazine pes IP_{av} values, and accounting for the multiple substitution of tetraalkylhydrazines using eq 2,[2c] where (LS,90°) refers to least-square values from

$$X(R) = IP_{av}(RNHNH_2)/9.872 \qquad (1)$$

$$IP_i(calcd) = IP_{av}(LS,90°)\prod_R (X(R) \pm \Delta(LS,90°)/2) \qquad (2)$$

the observed vs. calculated methylated hydrazine plot and the plus sign gives IP_2. Using eq 1 and 2, a series

of 22 acyclic alkylated hydrazines gave an excellent straight line in an IP_i(obsd) vs. IP_i(calcd) plot, which had a standard deviation of 78 meV (44 points). Our procedure is empirically justified by the remarkable success of eq 1 and 2 in predicting the pes spectra of acyclic hydrazines. Improved fit could certainly be obtained by considering the slightly different θ values which are present for hydrazines of different substitution patterns, but this imposes a degree of confidence in knowing the crossover points which is probably greater than is presently justified.[4]

In this paper we consider some aspects of the use of pes for obtaining θ values of hydrazines.

Results and Discussion

Angle Dependence of Tetraalkylhydrazine Pes. The substantial substituent independence of acyclic hydrazine pes spectra certainly does not extend to cyclic compounds.[1,2] Since most of our work has been with tetraalkylhydrazines, we shall restrict our discussion to these compounds. The INDO predictions for the splittings of tetramethylhydrazine (idealized geometry) as a function of θ are shown in Table I as $\Delta_I(\theta)$ (the I is

Table I. Angle-Dependent Terms for Correlation of Ionization Potentials and θ for Tetraalkylhydrazines

θ, deg	$\Delta_I(\theta)$,[a] eV	$\Delta_{2.5}(\theta)$,[b] eV	$\delta I(\theta)$,[c] eV
0	3.083	2.172	0.275
10	2.944	2.074	0.249
30	2.231	1.572	0.154
60	0.999	0.704	0.035
80	0.133	0.094	0.011
90	0.354	0.249	0.004
100	0.863	0.608	0
120	1.823	1.284	0.045
140	2.585	1.821	0.214
160	3.184	2.244	0.429
170	3.423	2.412	0.527
180	3.548	2.500	0.581

[a] $\Delta_I(\theta) = E_1 - E_2$, where E_1 is the highest occupied MO (n_- for $\theta < 83°$, n_+ for $\theta > 83°$) and E_2 the other lone pair MO, from INDO calculations on tetramethylhydrazine in standard geometry. [b] $\Delta_{2.5}(\theta) = 0.705\Delta_I(\theta)$, used as a working curve for evaluation of θ from observed Δ. [c] $\delta I(\theta) = E_{av}(100°) - E_a(\theta)$.

for INDO). Not surprisingly, direct use of $\Delta_I(\theta)$ for prediction of θ gives unreasonable values. INDO overestimates the splitting, and $\Delta_I(\theta)$ must be scaled down to be useful. We have chosen to simply multiply $\Delta_I(\theta)$ by a constant to perform this scaling. Consideration of all of our data suggests that $\Delta(180°)$ is about 2.5 eV, so our working curve for estimation of angles from Δ values was obtained by multiplying $\Delta_I(\theta)$ by 0.705, giving the $\Delta_{2.5}(\theta)$ values listed in Table I.[5]

(4) The crossover point becomes crucial in fine adjustments of θ, and, for low Δ values, it is not clear whether one is on the high or low θ side of the crossover point.

(5) Rademacher[1b] has suggested using the notably simpler function for what we call Δ (he uses a sign change depending on whether n_+ or n_- is higher in energy), $\Delta E = 2.17 \cos \theta - 0.35$. Our scaling only differs significantly from his near $\theta = 0°$. $\Delta E = 0$ at 80.7°, compared to 83° for $\Delta_{2.5}$. On the low θ side $\Delta_{2.5}$ and ΔE differ by a maximum of 3° until Δ is >1.57 eV, and, on the high θ side, the use of $\Delta_{2.5}$ will lead to higher θ values by an amount which increases from 2.3° ($\Delta = 0$) to 5° at $\Delta = 1.37$, passes through a maximum of 9° at 2.25 eV, and then decreases ($\Delta E(180°) = (-)2.52$). The similarity of these functions suggests that fair accuracy might be expected for the derived θ values, since the methods of obtaining ΔE and $\Delta_{2.5}$ were rather different.

The INDO calculations also show that E_{av} depends upon θ, with an extremum near 100° (see Table I). Taking this into account, we examine using equations 3 and 4 for prediction of ionization potentials of tetra-

$$IP_i(\theta) = IP_{av}(\theta) \pm \Delta_{2.5}(\theta) \qquad (3)$$

$$IP_{av}(\theta) = 8.57 \prod_R X_R + \delta I(\theta) \qquad (4)$$

alkylhydrazines. It should be noted that $\delta I(\theta)$ is a positive number which is negligible (<0.035 eV) when $\Delta_{2.5}(\theta)$ is less than 1 (θ between 65 and 115°) but is a significant correction outside this range.

The $\delta I(\theta)$ term indicates that conformations with large Δ values should show higher values of IP_{av}. This was to us an nonintuitive result, and, since we were concerned that it might be an artifact of the tetramethylhydrazine calculation (since we simply rotated an all-skew 90° conformation to change θ, considerable steric interactions were likely), we sought additional evidence for the form of $\delta I(\theta)$. A proper check of this for tetramethylhydrazine would presumably involve energy minimization at each θ value, which we found neither attractive nor fiscally possible. As a check in the conclusion that IP_{av} increases with Δ, we offer calculations on hexahydrotetrazine in the diequatorial, diaxial conformation 1. Because of the molecular symmetry of

1
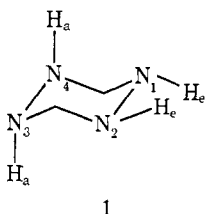
the conformation (C_2), the lone pair ionization potentials happen to be from orbitals which are essentially localized on either the N_1N_2 or the N_3N_4 hydrazine unit (which is not true of any of the other six conformers). The calculated energies were $E_1(A, n_+(N_1N_2)) = 10.623$, $E_2(B, n_-(N_3N_4)) = 11.137$, $E_3(A, n_+(N_3N_4)) = 12.664$, and $E_4(B, n_-(N_1N_2)) = 14.625$ eV. As expected, the N_1N_2 hydrazine which has θ near 180° has $n_+ > n_-$, and the ca. 60° θ N_3N_4 hydrazine shows $n_- > n_+$. The orbital energies are clearly affected by the presence of the second hydrazine in the molecule, but the ionization potentials are compared to each other intramolecularly, obviating the need for external standardization. Since E_{av} for the diaxial lone pair hydrazine N_1N_2 (-12.674) is substantially below that for the diequatorial N_3N_4 (-11.900), the large Δ N_1N_2 hydrazine is calculated to have 0.724 eV higher IP_{av}. These IP values are unscaled and are larger than would be expected for tetraalkylhydrazines, but since both this calculation and the ones on tetramethylhydrazine gave the result that IP_{av} should be higher when Δ is large, we are encouraged to believe that the tetramethylhydrazine result was not merely a steric artifact. This is unfortunate, since it will tend to cause IP_1 for large and small Δ conformers of the same molecule to overlap. This was the assignment made[1b,2b] for hexahydropyridazine pes spectra, which is now qualitatively justified on the basis of calculations. Experimentally, it is very difficult to locate IP_1 for a minor conformation accurately since it occurs under IP_1 for the major conformation, causing considerable error in estimation of its position.

Calculated Effect of Deviations from Tetrahedrality at Nitrogen. The correlations leading to eq 3 and 4 were carried out using INDO calculations on tetramethylhydrazine which was tetrahedral at nitrogen. To estimate the error one might reasonably expect to find in θ values derived using a $\Delta(\theta)$ working curve, one must consider the probability that all hydrazines are not going to have tetrahedral nitrogens ($\gamma = \angle RNR = \angle NNR = 109.5°$); the same $\Delta(\theta)$ curve, whatever its source, ought not to be applicable to all compounds. A microwave study on 1,1- and 1,2-dimethylhydrazine[6] gave $\gamma \approx 110 \pm 4°$, and, in a more recent investigation of methylhydrazine,[7] the problems in obtaining exact angles for hydrazines were discussed. A value near 113° was preferred for the NNC angle of methylhydrazine.[7] Although the microwave spectrum of tetrakis(trifluoromethyl)hydrazine has been interpreted as showing that this compound is essentially planar at nitrogen,[8a] the ir–Raman work of Durig and coworkers[8b] indicates that this was the result of a bad assumption. The good correlation between calculated and observed ionization potentials for the five methylated hydrazines assuming a constant geometry (tetrahedral, $\theta = 90°$) implies either that any geometrical changes are small enough to be ignored or that they happen to cancel errors in the calculations.

To attempt to assess the magnitude of the effect upon the ionization potentials expected for angle deformations at the nitrogens, we have chosen to employ INDO calculations on hydrazine itself. Although we wish to interpret tetraalkylhydrazine spectra especially, the increase in complexity (and cost) of the calculations is dramatic if four alkyl groups are present, and it is by no means apparent that additional useful information would result. Table II contains the results of INDO calculations for two degrees of symmetrical flattening (we kept $\angle NNH = \angle HNH = \gamma$), $\gamma = 113.5$ and $\gamma = 115.8°$, compared with these for tetrahedral hydrazine ($\gamma = 109.5$). Since $E_1 - E_2$ should correspond to (unscaled) Δ, and $-E_{av}$ to (unscaled) IP_{av} for hydrazine, we shall discuss results in terms of these quantities. The extreme splittings are predicted to increase by 23% ($\theta = 0$) and 5% ($\theta = 180°$) in flattening from $\gamma = 109.5°$ to $\gamma = 115.8°$, while the crossover point moves from $\theta = 85.5°$ ($\gamma = 109.5°$) to $\theta = 88.2°$ ($\gamma = 115.8°$). These are the changes expected, since completely planar hydrazine ($\gamma = 120°$) would have pure "lone pair" p orbitals, so $\Delta(0°) = \Delta(180°)$, crossover at $\theta = 90°$. The $\Delta(\theta)$ curves derived from these calculations would be essentially identical in the region of θ ca. 100–120°, since a rough "isosbestic point" occurs near 104°. As examples of the sorts of error which would be expected if the $\gamma = 109.5°$ $\Delta(\theta)$ curve were used to give θ of a flattened hydrazine, see Table III. Errors of >5° in θ would only result when θ is not between 55 and 150° for $\gamma = 113.5°$ and 70 and 140° for $\gamma = 115.8°$. It seems from these calculations that very large angle deviations should not occur between the nine acyclic tetraalkylhydrazines which showed nearly constant Δ values;[2c] since the crossover point should approach 90° as γ

(6) W. Beamer, *J. Amer. Chem. Soc.*, **70**, 2979 (1948).
(7) R. P. Lattimer and M. D. Harmony, *J. Chem. Phys.*, **53**, 4575 (1970).
(8) (a) L. S. Bartell and H. K. Higginbotham, *Inorg. Chem.*, **4**, 1346 (1965); (b) J. R. Durig, J. W. Thompson, and J. D. Witt, *ibid.*, **11**, 2477 (1972).

Table II. Results of INDO Calculations on N_2H_4. Showing the Effect of a Symmetrical Flattening at Nitrogen on the Lone Pair Orbitals

θ, deg	$-E_2 - E_1$(eV) for $\angle$(HNH) = $\angle$(NNH) = γ			$-E_{av}$ (eV) for $\angle$(HNH) = $\angle$(NNH) = γ		
	$\gamma = 109.5°$	$\gamma = 113.5°$	$\gamma = 115.8°$	$\gamma = 109.5°$	$\gamma = 113.5°$	$\gamma = 115.8°$
0	4.585	5.230	5.657	13.757	13.548	13.441
20	4.014	4.593	4.961	13.666	13.330	13.210
40	2.950	3.410	3.695	13.306	13.057	12.915
60	1.714	2.030	2.229	13.119	12.857	12.712
80	0.370	0.515	0.656	13.020	12.758	12.611
90	0.318	0.220	0.150	13.008	12.747	12.600
100	1.012	0.988	0.961	13.023	12.761	12.614
120	2.392	2.509	2.555	13.133	12.874	12.726
140	3.722	3.956	4.076	13.358	13.102	12.950
160	4.952	5.287	5.453	13.701	13.452	13.298
180	6.215	6.346	6.444	14.091	13.872	13.674
Crossover point[a]	85.5°	87.0°	88.2°			

[a] The θ where $E_2 - E_1$ is zero.

Table III. Deviations Predicted by INDO if the Tetrahedral N_2H_4 $\Delta E(\theta)$ Curve Is Used to Measure for Flattened N_2H_4

ΔE	$\theta_T,^a$ deg	$\theta_T - \theta$ ($\gamma = 113.5°$)	$\theta_T - \theta$ ($\gamma = 115.8°$)
4	20.3	11.1	15.7
3	39.3	6.7	10.4
2	55.5	5.0	7.4
1.5	63.2	3.8	6.1
1.0	70.6	3.0	5.0
0.5	78.1	2.5	3.9
0	85.5	1.5	2.7
0.5	92.6	1.0	1.7
1.0	99.8	0.4	0.7
1.5	107.0	−0.3	−0.4
2.0	114.3	−1.1	−1.4
3	129.1	−2.4	−3.5
4	144.6	−4.1	−5.7
5	161	−5.9	−8.3

[a] θ_T is $\theta(\gamma = 109.5°)$, the angle given by the curve calculated for N_2H_4 having tetrahedral nitrogens.

increases, the largest change that could be accounted for by flattening at nitrogen would be an increase in θ, but this would only tend to force the inner substituents toward each other. Although the nitrogens probably flatten, perhaps substantially, the true value of θ should not deviate very much from that given by $\Delta(2.5)$.

The calculations predict a decrease in IP_{av} as γ is increased, its magnitude being nearly independent of θ. For $\gamma = 113.5°$, the change predicted in IP_{av} ($\delta I(\theta)$) was 0.26 eV between $\theta = 60$ and 140°, decreasing to a minimum of 80% of this value at $\theta = 0°$. For $\gamma = 115.8°$, $\delta I(\theta)$ was 0.41 eV, dropping to a minimum of 78% of this figure at 0°. Although the calculations were for hydrazine itself, we will assume that the form of the changes is correct, and that θ(est) obtained from our $\Delta_{2.5}$ curve ought to be increasingly too low for θ(est) values near 0°, and increasingly too high near 180°, if the hydrazine is significantly flattened from the geometry of tetramethylhydrazine. Furthermore, these calculations predict that IP_{av} observed for a hydrazine flattened enough to cause deviations in θ(est) to be very far from the true value should be decreased by a measurable amount over what it would have been for the hypothetical unflattened compound.

Cyclic Dialkylhydrazines. Since only cyclic hydrazines of those so far investigated show large Δ values, we are particularly interested in being able to estimate IP_{av}

for such compounds. As the effects of changing methyl for another alkyl group in acyclic hydrazines were adequately described by the $X(R)$ value procedure, we have extended this method to cyclic substituents. From the spectra of the 1,1- and 1,2-dialkylhydrazines quoted in Table IV, we obtained the $X(R)$ values shown in Table

**Table IV.** Pes Spectra of Cyclic Dialkylhydrazines, Compared with Those of Dimethylhydrazines

Compound		IP_1	IP_2	Δ	IP_{av}
$\langle\rangle$NNH$_2$	2	8.82_8	9.87_5	1.04_7	9.35_2
$\langle\rangle$NNH$_2$	3	8.68_1	9.81_5	1.13_4	9.24_8
$\langle\rangle$NNH$_2$	4	8.63_1	9.81_3	1.18_2	9.22_2
Me$_2$NNH$_2$	5	8.88	10.31	1.24_6	9.50_5
$\langle\rangle$NH NH	6	9.15_8	9.78_0	0.62_2	9.46_9
$\langle\rangle$NH NH	7	8.64_1	9.49_2	0.85_1	9.06_7
MeNHNHMe	8	9.00	9.73	0.72_6	9.36_5

V by substitution into eq 5, where IP_{av} (LS, 90°) refers

$$X(R)^2 = IP_{av}(\text{obsd})/IP_{av}(LS,90°) \qquad (5)$$

to the value for the methylated hydrazine of like substitution, 9.468 eV for 1,1-dialkyl compounds and 9.332 eV for 1,2-dialkyl compounds. Since the Δ values observed for 2–7 are close to those for acyclic compounds, large differences in θ are not present, allowing the $\delta I(\theta)$ term to be ignored. We argue that 3–7 are expected to have angles (γ) reasonably close to those for acyclic hydrazines, so effects on IP_{av} due to changes in geometry at nitrogen should also be ignorable. It is worth noting that the IP_{av} values predicted from the $X(R)$ values of two ethyls, pyrrolidine (1,1-(CH$_2$)$_4$), and hexahydropyridazine (1,2-(CH$_2$)$_4$) all fall within 43 meV when these groups are incorporated in a tetraalkylhydrazine. The larger X values for azetidine (1,1-(CH$_2$)$_3$) and pyrazolidine (1,2-(CH$_2$)$_3$) groups suggest that there is a detectable "through bond" inductive

Table V. X(R) Values for Some Cyclic and Acyclic Alkyl Substituents

Hydrazine used[a]		X(R)[b]
CH₃—⋮—NHNH₂		1.0 (by definition)
CH₃CH₂—⋮—NHNH₂		0.9884
CH₂CH₂CH₂—⋮—NHNH₂		0.9786
(CH₃)₂CH—⋮—NNH₂		0.9751
CH₃(CH₂)₃—⋮—NHNH₂		0.9722
(CH₃)₃C—⋮—NHNH₂		0.9641
⟨NNH₂⟩	2	0.9938[c]
⟨NNH₂⟩	3	0.9883
⟨NNH₂⟩	4	0.9869
⟨NH–NH⟩	6	1.0073
⟨NH–NH⟩	7	0.9857
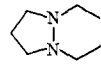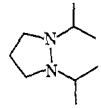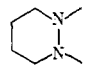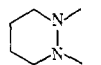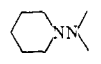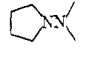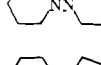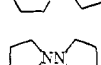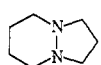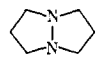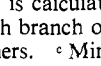
[a] The alkyl groups are set off by dotted lines. [b] Calculated by eq 1 or 5. [c] See text.

Table VI. Pes Spectra of Some Cyclic Tetraalkylhydrazines

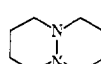| Compound		IP₁	IP₂	Δ	θ(est),[a] deg
	8[b]	7.777	10.078	2.301	163
	8[c]	8.325	9.135	0.810	106
	9	8.060	8.935	0.875	107
	10	7.807	7.799	0.992	111
	11[b]	7.809	10.132	2.233	164
	11[c]	?	8.855	?	
	11	8.092	8.634	0.542	98
	13	7.972	8.556	0.584	99
	14	7.892	8.408	0.516	97
	15	7.951	8.505	0.554	98
	16	7.888	8.588	0.700	102
	17	7.608	9.915	2.307	163
	18	7.634	9.952	2.318	164
	19	7.874	9.447	1.573	30

[a] θ is calculated from $\Delta_{2.5}$ (Table I) and involves assumption of which branch of the $\Delta(\theta)$ curve is to be used. [b] Major of two conformers. [c] Minor of two conformers.

effect being observed, operating through three methylene units. The difference in $X(1,1\text{-}(CH_2)_3)$ and $X(1,2\text{-}(CH_2)_3)$ predicts a significant (0.23 eV) difference in IP_{av} if these groups are incorporated into a tetraalkylhydrazine. The obvious bond angle change in the $1,1\text{-}(CH_2)_3$ ring is a likely candidate for the cause of this difference.

Cyclic Tetraalkylhydrazines. In Table VI, pes data for 12 cyclic tetraalkylhydrazines containing groups for which X(R) has been independently determined using mono- and dialkylhydrazine spectra are presented. For 1,2-dimethylpyrazolidine (**8**) and 1,2-dimethylhexahydropyridazine[2a, 1b] (**11**), two conformers were observed in the spectrum, although in the latter case, our deconvolution procedure did not manage to locate IP_1 of the minor conformer successfully. Also presented in Table VI are θ(est) angles obtained using $\Delta_{2.5}$. In a check for reasonability of using X(R) for cyclic compounds, values of IP_{av}(calcd) computed from eq 3 and 4 are presented in Table VII and compared with experiment and the corresponding values for nine acyclic hydrazines. There is relatively little to choose between the fit to IP_{av}(calcd) to IP_{av}(obsd) for acyclics and cyclics with $\Delta < 1$ eV (root mean square deviation is 48 meV for the nine acyclic and 52 meV for the eight cyclic compounds). The values of IP_{av}(calcd) are significantly worse for the five cyclic compounds for which Δ is large (**8, 11, 17–19**). It is clear that eq 4 does not give useful IP_{av}(calcd) values for these compounds. The most obvious source of error is $\delta I(\theta)$ which is not only completely unscaled but has a rather arbitrary definition. Unfortunately, the value of $\delta I(\theta)$ is not the only problem, since the deviation values are large with both negative and positive signs—altering $\delta I(\theta)$ could "help" one set but only at the expense of the other.

The obvious breakdown for eq 4 for predicting IP_{av} of tetraalkylhydrazines which have large Δ values is perhaps not very surprising. Structural constraints (rings) are required to force θ to a value deviating greatly from 90°, and it seems reasonable that distortion from tetrahedral geometry at the nitrogens might result.

The calculations on flattened hydrazine indicate that IP_{av} should be sensitive to such angle deformations. These calculations also suggest that when eq 4 does not suffice to calculate IP_{av}, that the θ values obtained from $\Delta_{2.5}(\theta)$ ought to be significantly affected. Our most important conclusion from consideration of the utility of eq 4 is that $\Delta_{2.5}(\theta)$ probably becomes uncreasingly inaccurate as Δ becomes greater than 1 eV. The magnitude of these deviations must await accurate structure determinations.

It should be pointed out that the sign observed for deviation in the high Δ compounds of Table VII, pyrazolidines showing "too low" ionization potentials and hexahydropyridizines "too high" ones, are similar to those observed for electrochemical $E_{1/2}$ values.[10] This raises the possibility that the energies of the *stable* form of the radical cation, which certainly affect the $E_{1/2}$ values, are also reflected in the observed IP_{av} values.

Table VII. Comparison of IP_{av}(obsd) and IP_{av}(calcd) Values for Some Tetraalkylhydrazines

Compound	IP_{av}(obsd)	IP_{av}(calcd)[a]	Dev[b]
Acyclics[c]			
Me_2NNMe_2	8.55	8.57	$+0.020$
$Me_2NNMeEt$	8.45	8.47	$+0.020$
Me_2NMe-i-Pr	8.36_0	8.35_7	-0.003
Me_2NNMe-n-Bu	8.38_5	8.33_2	-0.053
Me_2NNEt_2	8.36_5	8.37_2	$+0.00_7$
Et_2NNEt_2	8.19_5	8.17_9	-0.01_6
Et_2NN-i-Pr_2	8.12_6	8.01_8	-0.11_1
t-$BuMeNNMe$-t-Bu	7.92_0	8.96_6	$+0.046$
i-Pr_2NNMe-i-Pr	7.89_5	7.94_6	$+0.05_1$
Cyclics ($\Delta < 1$)			
8 ($\Delta = 0.8$)	8.73_0	8.70_5	-0.025
9	8.49_8	8.50_7	$+0.00_9$
10	8.30_3	8.28_6	-0.017
12	8.36_3	8.34_7	-0.01_6
13	8.26_4	8.37_1	$+0.107$
14	8.15_0	8.13_0	-0.02_0
15	8.22_8	8.15_4	-0.074
16	8.23_8	8.17_6	-0.06_1
Cyclics ($\Delta > 1$)			
8 ($\Delta = 2.3$)	8.92_8	9.15_4	$+0.226$
11 ($\Delta = 2.3$)	8.87_1	8.79_6	-0.07_5
17	8.76_1	8.55_1	-0.21_0
18	8.79_3	8.91_4	$+0.12_1$
19	8.66_0	8.97_9	$+0.319$

Conclusion

This work investigates the utility of using the lone pair–lone pair splitting Δ to estimate the lone pair–lone pair dihedral angle θ for tetraalkylhydrazines. A semi-empirical working function $\Delta_{2.5}(\theta)$ is suggested to relate these quantities. This function was derived using INDO calculations on tetramethylhydrazine which was tetrahedral at nitrogen. Consideration of the calculated effects of bond angle deformations at nitrogen on both Δ and IP_{av} lead to the conclusion that use of $\Delta_{2.5}(\theta)$ should become increasingly risky when Δ exceeds 1 eV.

The utility of a semiempirical function like $\Delta_{2.5}(\theta)$ for determination of conformation of hydrazines can only rest upon the successful application of this method for conformational analysis. We consider the conformational information so obtained for several five- and six-membered ring hydrazines in detail in the following paper.

Experimental Section

The compounds employed are known ones, the preparation of which has been described elsewhere.[9,10] The photoelectron spectroscopy experiments and the calculations used have also been described previously.[2c]

(9) N-Nitrosoazetidine was prepared by the method of C. L. Bumgardner, K. S. McCallum, and J. P. Freeman, J. Amer. Chem. Soc., **83**, 4417 (1961), and was reduced to N-aminoazetidine (2) using lithium aluminum hydride (see J. P. Freeman, D. G. Pucci, and G. Binsch, J. Org. Chem., **37**, 1894 (1972)).

(10) S. F. Nelsen and H. J. Hintz, J. Amer. Chem. Soc., **94**, 7108 (1972).

Photoelectron Spectra of Hydrazines. V. Pyrazolidine and Hexahydropyridazine Derivatives

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Abstract: The photoelectron spectra of 28 1,2-cycloalkylhydrazines containing pyrazolidine, hexahydropyridazine, and 1,2,3,6-tetrahydropyridazine structures are reported and discussed in terms of the conformational information supplied by the spectra. The direction and amount of torsion in 2,3-diazabicyclo[2.2.1]heptyl and pyrazolidine rings are easily extracted from the data. In some cases, more than one conformation was observed.

The conformations of cyclic hydrazines have been fairly intensively studied by several groups. Low temperature nmr spectroscopy has been used for distinguishing cis and trans distribution of nitrogen substituents in cyclic compounds and dynamic nmr has been used for measuring the activation energies for conformational interconversions,[1] but nmr has not yet yielded quantitative information about the geometry of hydrazines. The "R value" technique[2] has been successfully applied to a number of six-membered ring heterocycles but has not been used for hexahydropyridazines. Dipole moment studies by Katritzky and coworkers[3] have led to the important conclusion that some of the nmr work was misinterpreted because some nitrogen and ring inversions are much easier to "freeze out" than others.

As has been developed in previous papers by our group[4] and by Rademacher,[5] photoelectron spec-

(1) (a) J. E. Anderson, J. Amer. Chem. Soc., **91**, 6374 (1969), and references therein; (b) J. M. Lehn, Forschr. Chem. Forsch., **10**, 311 (1970); (c) Tetrahedron, **25**, 657 (1969).

(2) (a) J. B. Lambert, Accounts Chem. Res., **4**, 87 (1971); (b) J. B. Lambert, J. J. Papay, E. S. Magyar, and M. K. Newberg, J. Amer. Chem. Soc., **90**, 4458 (1973).

(3) R. A. Y. Jones, A. R. Katritzky, and R. Scattergood, Chem. Commun., 644 (1971).

(4) (a) S. F. Nelsen and J. M. Buschek, J. Amer. Chem. Soc., **95**, 2011 (1973); (b) S. F. Nelsen, J. M. Buschek, and P. J. Hintz, ibid., **95**, 2013 (1973); (c) S. F. Nelsen and J. M. Buschek, ibid., **96**, 2392 (1974); (d) ibid., **96**, 6982 (1974).

(5) (a) P. Rademacher, Angew. Chem., **85**, 410 (1973); (b) Tetrahedron Lett., 83 (1974).