of hydrazine and equilibrated hydrazinium cation are very different.[14] There are also obvious differences of phase.

Acknowledgment. We thank the National Science Foundation for generous support of this research (GP-34488X) and the major instrument program of NSF for funds used in purchasing the IEE.15 spectrometer.

[14] S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, **93**, 7105 (1971).

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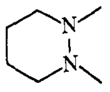
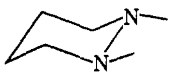
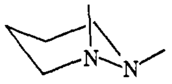
Photoelectron Spectra of Hydrazines. II. Conformations of Hexahydropyridazines

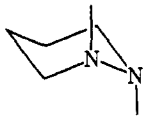
Sir:

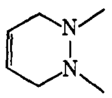
The conformations of six-ring hydrazines are still in dispute. Anderson[1] suggested from low-temperature nmr studies that 1,2-dimethylhexahydropyridazine (**1**) had only the equatorial, equatorial (e,e) conformation (**1a**) in observable concentration, assuming that both nitrogen and ring inversion were frozen out at −120° on the basis of analogy with 1,2-dimethyl-1,2,3,6-tetrahydropyridazine (**2**), to which he assigned the axial, equatorial (a,e) conformation **2a**, because he could observe two "freezing" processes (one for N inversion and one for ring flipping), and nonequivalent *N*-methyl signals of equal area at low temperature. Jones, Katritzky, and coworkers[2] disputed these interpretations.


1


1a


1b


1c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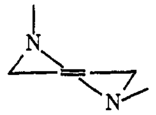
2a

They noted that the nmr spectrum of **1** could be a mixture of **1a**, **1b**, and **1c** if they interconvert at −120°, by a combination of ring flips and nitrogen inversions which do not force vicinal methyls past each other, accounting for only observing a single *N*-methyl peak. Higher barriers to conformer interconversion, according to Katritzky and coworkers,[2b] are to be expected only when methyl groups must pass each other in the inversion process. From dipole moment measurements on **1** and its 4,4-dimethyl derivative and an equilibrium constant measured at −90°, they arrived at the remarkable conclusions that **1a**, **1b**, and **1c** are in a 30:34:36 mixture at room temperature.

Since a photoelectron spectra (pes) experiment has a time scale comparable to those of ir and uv, if **1** is a mixture of conformers, one will observe the superposition of their photoelectron spectra.

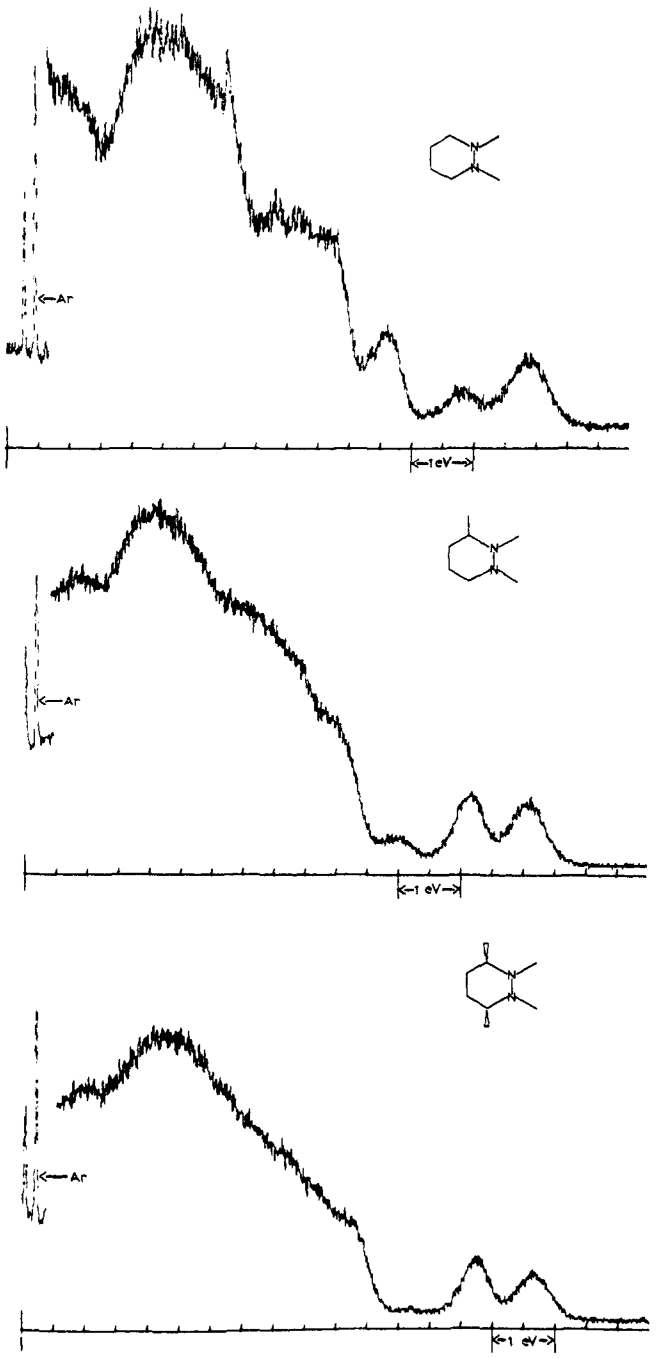

Figure 1. Photoelectron spectra of **1**, **5**, and **4**, illustrating the variation in the relative intensities of I_{p2} and I_{p3}.

Since **1a** has an antihydrazine configuration ($\theta \sim 180°$), its lone pair–lone pair splitting should be quite large compared to those of **1b** and **1c** ($\theta \sim 60°$) and more than two "lone pair" ionizations ought to be observed. The pes of **1** (Figure 1) does show three peaks in the "lone pair" ionization region, in contrast to the bicyclic hydrazines, which give only the two expected peaks.[3] The peak positions and approximate relative areas of these peaks are given in Table I. We assume that ionizations from at least two conformations are observed, with the lowest ionizations from each overlapping as peak 1. The peak separations are consistent with **1a** being the principal conformation (Δ = 2.31) in the vapor phase at room temperature, with **1b** and/or

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[1] J. E. Anderson, *J. Amer. Chem. Soc.*, **91**, 6374 (1969).

[2] (a) R. A. Y. Jones, A. R. Katritzky, and R. Scattergood, *Chem. Commun.*, 644 (1971); (b) R. A. Y. Jones, A. R. Katritzky, D. L. Ostercamp, K. A. F. Record, and A. C. Richards, *ibid.*, 644 (1971).

[3] S. F. Nelson and J. M. Buschek, *J. Amer. Chem. Soc.*, **95**, 2011 (1973).

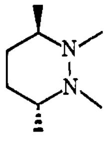
Table I. "Lone Pair" Pes Ionizations for Hexahydropyridazine Derivatives

Compound	I_{p1}, eV (area[a])	I_{p2}, eV (area[a])	I_{p3}, eV (area[a])	$\Delta_{1,2}$[b]	$\Delta_{1,3}$[c]
1	7.77 (2.6)	8.86 (1)	10.08 (2.1)	1.09	2.31
3	7.78 (0.9)	8.63 (1)	9.76 (0.02)	0.85	1.98
4	7.82 (0.9)	8.68 (1)	9.76 (0.04)	0.86	1.94
5	7.81 (1)	8.77 (1)	9.96 (0.2)	0.98	2.15

[a] Estimated area under the ionization peak relative to that of peak 2 (taken as 1.00); since peaks 1 and 2 overlap badly, these estimates are quite crude. [b] $I_{p2} - I_{p1}$. [c] $I_{p3} - I_{p1}$.

1c (Δ = 1.09) also being easily detectable. Although the areas under pes peaks may not necessarily be exactly proportional to the number of electrons ionized[4] and future work will be necessary to see how quantitative such data can be made, the presence of both types of conformers and preponderance of the e,e conformer **1a** seems to us the most reasonable interpretation of the data.

In contrast, *trans*-3,6-dimethyl-1,2-dimethylhexahydropyridazine (**3**) gave large pes peaks separated by 0.85 eV and only a tiny peak 1.98 eV higher than I_{p1} (area relative to I_{p2} about 0.02), which is consistent with very little of the e,e conformation **3a** being present.



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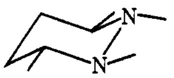
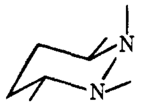
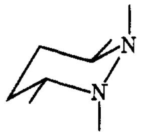


3a



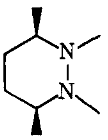
3b



3c

The nmr spectrum of **3** in CF_2Cl_2 at −120° showed two equal NCH_3 singlets (δ 2.34, 2.10) and two equal intensity $CHCH_3$ doublets (δ 0.97, 0.91), consistent only[5] with **3b**. Conformations **3a**, **3b**, and **3c** cannot interconvert by processes which avoid forcing vicinal methyl groups past each other, and so these conformations should be "frozen out" at low temperature, in contrast to **1a**–**1c**.[2] We observed only a single asymmetric conformation, which cannot be **3a** or **3c**. The nmr spectrum of **3** is consistent with the pes; **3b** is almost exclusively present.

The *cis*-tetramethyl compound **4** also showed only a tiny pes peak attributable to the e,e conformation **4a**, suggesting that **4b** is the major conformation present. Here we also saw only one conformation by low-temperature nmr, but, since the molecule lacks any symmetry, a structure could not be assigned unambiguously. The pes of **5** shows a more substantial amount of the large Δ (e,e) conformer relative to e,a conformers of either **3** or **4**; for **5** the relative areas were 0.2:1. The nmr spectrum showed two sets of $CHCH_3$ doublets in 70:30 ratio in $CDCl_3$ (−60°) and 90:10 ratio in CF_3Cl_2 (−65°). We did observe another rate process starting to "freeze out" at very low temperatures, but were unable to obtain resolved spectra at the low-temperature limit. The lack of symmetry again prevents us from assigning conformational structures from the nmr data, but the fact that two important conformations were observed by nmr as well as pes is consistent with our assumption that the relative amounts of conformations present may be estimated by areas under pes curves is at least semiquantitatively correct.



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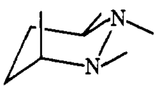
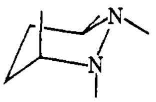
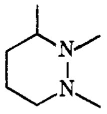


4a



4b



5

Our pes and nmr data agree satisfactorily, where testable, and show that a definite preference for the axial, equatorial distribution of *N*-methyl substituents in the hexahydropyridazene system occurs in the presence of a methyl group on the 3 position, although the equatorial, equatorial disposition is preferred without a flanking methyl group. The pes and nmr data complement each other and show that pes can be useful for conformational analysis, particularly in compounds of lower symmetry, and also because the experiment is performed in the absence of solvation effects.

Acknowledgment. We thank the National Science Foundation for generous support of this research (GP-34488) and the major instrument program of NSF for funds used in purchasing the IEE.15 and XL-100 spectrometers used in this work.

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(4) J. A. Kisinger and J. W. Taylor, *Int. J. Mass Spectrom. Ion Phys.*, **10** (4), 445 (1973), and references therein.

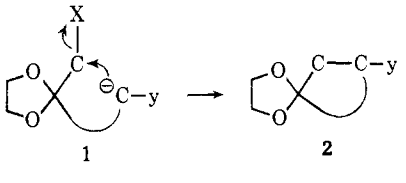
(5) We rule out structures with 1,3 diaxial methyl–methyl interactions as reasonable possibilities throughout.

Haloketal Cyclization. A General Method for the Synthesis of Functionalized Cis Bicyclic Ketones

Sir:

Cyclization reactions are especially valuable when the resulting rings bear functional groups in predictable relationships. When they are used to fuse a new ring onto a preexisting one ("annelation"), it is, of course, desirable that they lead to specific and predictable stereochemistry.

We now report a new, apparently general, reaction which meets both requirements. This is illustrated schematically by **1** to **2**



1 **2**