

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

Compound	$IP_{av}(\text{obsd})$	$IP_{av}(\text{calcd})^a$	$Dev^b$
Acyclics <sup>c</sup>			
Me <sub>2</sub> NNMe <sub>2</sub>	8.55	8.57	+0.020
Me <sub>2</sub> NNMeEt	8.45	8.47	+0.020
Me <sub>2</sub> NMe- <i>i</i> -Pr	8.360	8.357	-0.003
Me <sub>2</sub> NNMe- <i>n</i> -Bu	8.385	8.332	-0.053
Me <sub>2</sub> NNEt <sub>2</sub>	8.365	8.372	+0.007
Et <sub>2</sub> NNEt <sub>2</sub>	8.195	8.179	-0.016
Et <sub>2</sub> NN- <i>i</i> -Pr <sub>2</sub>	8.126	8.018	-0.111
<i>t</i> -BuMeNNMe- <i>t</i> -Bu	7.920	8.966	+0.046
<i>i</i> -Pr <sub>2</sub> NNMe- <i>i</i> -Pr	7.895	7.946	+0.051
Cyclics ( $\Delta < 1$ )			
8 ( $\Delta = 0.8$ )	8.730	8.705	-0.025
9	8.498	8.507	+0.009
10	8.303	8.286	-0.017
12	8.363	8.347	-0.016
13	8.264	8.371	+0.107
14	8.150	8.130	-0.020
15	8.228	8.154	-0.074
16	8.238	8.176	-0.061
Cyclics ( $\Delta > 1$ )			
8 ( $\Delta = 2.3$ )	8.928	9.154	+0.226
11 ( $\Delta = 2.3$ )	8.871	8.796	-0.075
17	8.761	8.551	-0.210
18	8.793	8.914	+0.121
19	8.660	8.979	+0.319

## Conclusion

This work investigates the utility of using the lone pair–lone pair splitting  $\Delta$  to estimate the lone pair–lone pair dihedral angle  $\theta$  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  $\Delta$  and  $IP_{av}$  lead to the conclusion that use of  $\Delta_{2.5}(\theta)$  should become increasingly risky when  $\Delta$  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.<sup>9,10</sup> The photoelectron spectroscopy experiments and the calculations used have also been described previously.<sup>20</sup>

**Acknowledgment.** We thank the National Science Foundation for support of this work, both through a research grant and the Major Instrument programs.

(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,<sup>1</sup> but nmr has not yet yielded quantitative information about the geometry of hydrazines. The “*R* value” technique<sup>2</sup> 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<sup>3</sup> 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<sup>4</sup> and by Rademacher,<sup>5</sup> photoelectron spec-

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

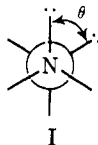
(1) (a) J. E. Anderson, *J. Amer. Chem. Soc.*, **91**, 6374 (1969), and references therein; (b) J. M. Lehn, *Fortschr. Chem. Forsch.*, **10**, 311 (1970); (c) *Tetrahedron*, **25**, 657 (1969).

(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).

(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).

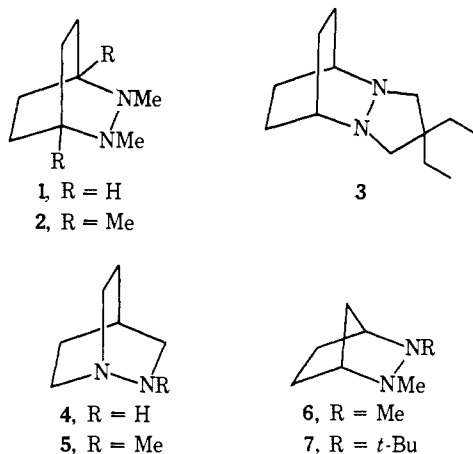
troscopy (pes) seems promising for measurement of a particularly useful structural parameter, the lone pair-lone pair dihedral angle  $\theta$  (see I), because of the sensi-



tivity of the lone pair-lone pair splitting,  $\Delta$ , to  $\theta$ . A semiempirical working curve,  $\Delta_{2,s}(\theta)$ ,<sup>4d</sup> which hopefully will allow determination of  $\theta$  from the  $\Delta$  measured by pes, has been suggested.<sup>6</sup> In this paper we consider the conformational information derived from the pes of cyclic tetraalkylhydrazine containing five- and six-membered rings and compare our results with those derived by other methods.

## Results and Discussion

**1. Bridged Bicyclic Hexahydropyridazine Derivatives.** We discuss these bicyclic compounds first because their structures rule out most conformations, and work on **6** and similar compounds showed conclusively that **1**, **2**, **6**, and **7** are trans dialkylated.<sup>1a</sup> Our data are



presented in Table I, along with  $\theta(\text{est})$ , the value of  $\theta$  obtained from the  $\Delta_{2,s}(\theta)$  curve.

**Table I.** Photoelectron Spectral Data for Bridged Bicyclic Hexahydropyridazine Derivatives

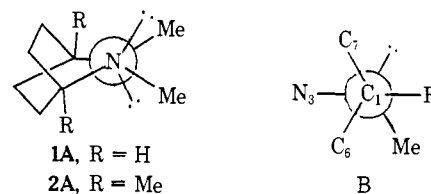
Compound	IP <sub>1</sub> , <sup>a</sup> eV	IP <sub>2</sub> , <sup>a</sup> eV	$\Delta$ , <sup>b</sup> eV	$\theta(\text{est})$ , <sup>c</sup> deg
<b>1</b>	7.46	9.28	1.82	140
<b>2</b>	7.43	8.89	1.46	126
<b>3</b> (major)	6.93	9.25	2.32	0
<b>3</b> (minor)	<i>d</i>	8.28		
<b>4</b>	8.52	9.25	0.73	
<b>5</b>	8.02	8.53	0.51	66
<b>6</b>	7.66	9.44	1.78	139
<b>7</b>	7.33	9.28	1.95	146

<sup>a</sup> Vertical ionization potentials. <sup>b</sup> IP<sub>2</sub> - IP<sub>1</sub>. <sup>c</sup> Estimated using  $\Delta_{2,s}(\theta)$ . <sup>d</sup> Obscured by IP<sub>1</sub> of the major conformation, presumably within 0.3 eV of 6.93 eV.

The 360 meV decrease in  $\Delta$  observed when **1** is methylated at the bridgeheads is particularly interesting

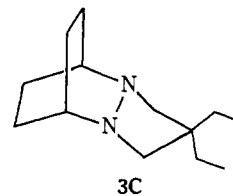
(6) Our working curve ( $\Delta_{2,s}(\theta)$ ) does not differ very substantially from Rademacher's (ref 5), although rather different assumptions went into constructing it. See ref 4d for a discussion of the minor differences. Our pes data agree well with those of Rademacher for the same compounds.

since similar structural changes in acyclic hydrazines do not change  $\Delta$ .<sup>4c</sup> Because of the bicyclic structure and the trans consideration of the *N*-methyl groups inferred from the nmr of the unsaturated compounds<sup>1a</sup> and similar compounds,  $\theta$  must be about 120° unless the bicyclooctyl system is torsionally twisted. Force-field calculations on the parent hydrocarbon have indicated that a  $\pm 10^\circ$  torsional twist affects the energy by less than 0.3 kcal/mol.<sup>7</sup> For **1**, a torsional twist to lower the *N*-methyl-methylene bridge steric interaction is expected, giving torsion in the sense shown in **1A** and



raising  $\theta$  above 120°. The observed  $\theta(\text{est})$  value of 140° is consistent with the expected direction of twist, and the size of the deformation seems plausible to us. Bridgehead methyl substitution to give **2** lowers  $\theta(\text{est})$  to 126°. The reduction of bicyclooctyl torsion in **2** is qualitatively to be expected, since torsion decreases the Me-C<sub>1</sub>N<sub>2</sub>-Me dihedral angle from the 60° for the untwisted form, causing an increasingly destabilizing C-methyl, N<sub>2</sub>-Me steric interaction. This is illustrated in the Newman projection along the C<sub>1</sub>-N<sub>2</sub> bond shown as **B**, where R = H for **1** and R = Me for **2**. The observed 126°  $\theta(\text{est})$  value encourages us that  $\theta(\text{est})$  is fairly accurate, even for **1** and **2**, which have rather large  $\Delta$  values.

The pes of **3** had a small peak between the two major ionization peaks, which we interpret as a small amount of a second conformation, with IP<sub>1</sub> for the minor conformation presumably obscured by that of the major conformation. The observed  $\Delta$  for the major conformation corresponds to  $\theta(\text{est})$  of either 0 or 164°. We rule out the latter as unreasonable, since it would require a huge torsional twist in the bicyclooctyl group. The pes  $\theta(\text{est})$  value therefore suggests that **3** exists cis fused, with  $\theta = 0^\circ$ . Unfortunately, the low temperature proton nmr of **3** did not have sufficient resolution to verify the cis fusion (the ethyl group chemical shifts should be different), but we argue that cis fusion is really expected for **3**, by comparison with 1,5-diazabicyclo[3.3.0]octane (see section 2), which also has a pyrazolidine ring fused to a ring which cannot torsionally twist extensively. We propose that the major conformation for **3** is **3C**, with the pyrazolidine ring in

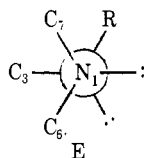


the envelope conformation having the quaternary carbon as the flap carbon, forcing the bicyclooctyl system to be eclipsed and  $\theta$  to be 0°. This arrangement should minimize steric interactions near the quaternary

(7) E. M. Engler, L. Chang, and P. v. R. Schleyer, *Tetrahedron Lett.*, 2525 (1972).

carbon (see section 2 for discussion of the same effect in 1,5-diazabicyclo[3.3.0]octanes, where the situation is clearer because we also have the compound lacking the quaternary carbon).

A  $60^\circ$   $\theta$  value is expected for **4** and **5** in the absence of bicyclooctyl torsion, as is illustrated in E, the projection



along the  $N_1-N_2$  axis. One expects torsion to decrease the  $N$ -methyl- $C_7H_2$  interaction, which should increase  $\theta$  slightly. The  $\theta(\text{est})$  value for **5** is entirely in line with these expectations. We do not have a good idea of the correlation of  $\Delta$  with  $\theta$  for trialkylhydrazine, but, since trialkylhydrazines probably have a larger splitting than a tetraalkylhydrazine at the same  $\theta$ ,<sup>4c</sup> the  $\theta(\text{est}) = 59^\circ$  value obtained using  $\Delta_{2.5}(\theta)$  is probably somewhat low.

The  $\theta(\text{est})$  values in Table I for the diazanorbonyl derivatives, **6** and **7**, are unreasonably high, since it is clear that less torsional twisting is expected for the [2.2.1] system<sup>8</sup> than for a [2.2.2] system, and  $\theta(\text{est})$  for **1** is  $140^\circ$ . We believe that angle deformations at the nitrogens of **6** and **7** are too great to allow use of  $\Delta_{2.5}(\theta)$  without introducing error. The increase in  $\Delta$  for **7** compared to **6** is unlikely to be entirely caused by a change in  $\theta$ , since the *tert*-butylated nitrogen of **7** is undoubtedly flattened by the substantial steric interactions of the attached groups, and flattening should increase  $\Delta$ .<sup>4d</sup> We believe that finding  $\theta(\text{est})$  values which are fairly clearly incorrect for **6** and **7** should caution one against expecting a single function to work for both unstrained and strained hydrazines, although Rademacher's data for bisaziridine<sup>5</sup> clearly do fit well.

**2. Pyrazolidine Derivatives.** The pes data for the nine pyrazolidine derivatives we have run appear in Table II.

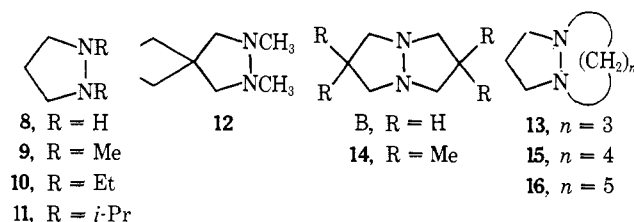


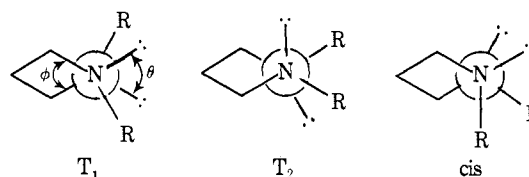
Table II. Photoelectron Spectral Data for Some Pyrazolidine Derivatives

Compound	IP <sub>1</sub> , eV	IP <sub>2</sub> , eV	L, eV	$\theta(\text{est})$ , deg
<b>8</b>	9.16	9.78	0.62	
<b>9(A)</b>	7.78	10.08	2.30	163
<b>9(B)</b>	8.33	9.14	0.81	106
<b>10</b>	8.06	8.94	0.87	107
<b>11</b>	7.81	8.80	0.99	111
<b>12</b>	7.59	9.997	2.38	168
<b>13</b>	7.87	9.45	1.57	30
<b>14</b> (major)	7.53	9.74	2.21	0
<b>14</b> (minor)	~7.53 sh	9.16	~1.6	~27
<b>15</b>	7.63	9.95	2.32	164
<b>16</b> (major)	7.58	9.34	1.76	138
<b>16</b> (minor)	Obscured	8.28		

(8) For a discussion of torsion in bicyclo[2.2.1]heptyl systems, see C. Altona and M. Sundaralingam, *J. Amer. Chem. Soc.*, **92**, 1995 (1970).

Two types of conformations are clearly represented for the monocyclic compounds **8**–**12**, one with a large splitting and one with a small one, although only for **9** were we able to observe both in a single compound. Although it is tempting to ascribe one to a *cis* conformation and one to a *trans* conformation one would really expect *trans* alkyl groups for all of these compounds on steric grounds, although this has only been proven by nmr for **12**. The large  $\Delta$  conformation, then must be *trans*, but when the *N*-alkyl substituent is increased in size from methyl to isopropyl, another conformation becomes more favored; it cannot reasonably be *cis*, which is obviously more sterically hindered.

There are two reasonable *trans* conformations for **8**–**12**, which differ in their direction of five-membered ring torsion ( $\phi$ ) and are shown below as  $T_1$  and  $T_2$ .



If the nitrogens are close to tetrahedral,<sup>9</sup>  $\theta$  for  $T_1$  should be close to  $120 - \phi$ , and for  $T_2$ ,  $\theta - (120 + \phi)$ , where  $\phi$  is the  $C_3N_2N_2C_3$  ring torsional angle. We assign the major ( $\Delta = 2.3$ ) conformation of **9** to  $T_2$ , and the minor ( $\Delta = 0.8$ ) conformation to  $T_1$ .<sup>10</sup> It is quite reasonable that 4,4-diethyl substitution (in **12**) would destabilize  $T_1$ , which has two 1,3-methyl,ethyl interactions which are relieved in  $T_2$ . The change from  $T_2$  being readily observable from **9** to  $T_1$  being the only observed conformation for **10** and **11** surprised us on qualitative grounds. The  $T_2$   $R_1-N_1, N_2-R_2$  dihedral angle is predicted to be about  $(120 - \phi)^\circ$ , while the  $R_1-N_1, N_2-C_3$  dihedral angle of  $T_1$  is also  $(120 - \phi)^\circ$ , but two such interactions are present. We believe the dilemma of how the  $T_1$  conformation, with two serious steric interactions, favored when R is larger than methyl is solved by consideration of the  $\theta(\text{est})$  values. The  $\phi$  value obtained from  $\theta(\text{est})$  is significantly larger for **9**- $T_2$  ( $43^\circ$ ) than for **9**- $T_1$  ( $14^\circ$ ), which would require that the steric interaction between the *N*-alkyl substituents in  $T_1$  is in fact more serious than the *N*-alkylmethylene interaction in  $T_2$ . It is, however, difficult for us to rationalize such a large  $\phi$  value as  $43^\circ$  for **9**- $T_2$ ; perhaps deformations at the nitrogens are large enough to cause serious error in applying  $\Delta_{2.5}(\theta)$ . Nevertheless, the position of the  $T_1 \rightleftharpoons T_2$  equilibrium as alkyl group size is changed is consistent with the relative sizes of  $\phi$  given by the pes data. It should also be pointed out that the  $T_1$  conformation could be favored

(9) Since strain in a five-membered ring system is known to be taken up almost exclusively in the bond angles, we have tried to see what would be expected for a pyrazolidine ring having  $R(\text{NN}) = 1.45$ ,  $R(\text{CN}) = 1.47$ , and  $R(\text{CC}) = 1.54$  Å. Assuming the angle strain to be roughly equally distributed, we obtained  $\angle N_1N_2C_3 = 109.5^\circ$ ,  $\angle N_2C_3C_4 = 105.9^\circ$ , and  $\angle C_3C_4C_5 = 106.5^\circ$ ,  $\phi = 17.5^\circ$ , ignoring all other factors.  $\angle N_1N_2C_3$  cannot be lowered without decreasing  $\angle N_2C_3C_4$  even more than it is above, and increasing it even  $1.5^\circ$  is impossible without increasing bond lengths. We conclude that tetrahedral geometry at nitrogen is not a bad approximation for unstrained pyrazolidines.

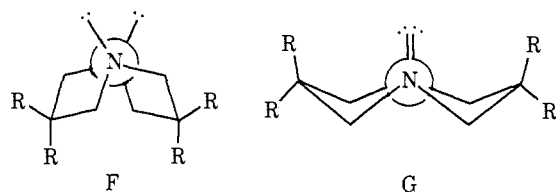
(10) This assignment agrees with Rademacher's<sup>5b</sup> "equatorial" and "diaxial" assignment, except that he chose the other branch of  $\Delta E(\theta)$  curve, giving  $\theta$  substantially below  $90^\circ$  for the "diaxial" conformer.

electronically,<sup>11</sup> because of the  $\theta$  value being closer to  $90^\circ$ .

The increase in  $\theta(\text{est})$  observed for the  $T_1$  conformers of **9**, **10**, and **11** seems reasonable on qualitative grounds. Larger R groups might be expected to enlarge the  $C_3-N_2$ ,  $N_1-R$  angle, increasing  $\theta$ . It is plausible that the nitrogens would flatten as R is increased in size, but a substantial flattening should lead to a decrease in  $IP_{\text{av}}$  beyond that expected for simply homologating the R group, no such effect was observed.<sup>4d</sup> Since  $\Delta(\theta)$  is calculated to be nearly insensitive to flattening at nitrogen near  $\theta = 110^\circ$  anyway,<sup>4d</sup> the  $\theta(\text{est})$  values for **9-11** are likely to be our most accurate ones, and presumably reflect changes in  $\phi$  as the size of the substituent is enlarged.

Pyrazolidine itself (**8**) shows a smaller splitting than any of the substituted compounds and even smaller than 1,2-dimethylhydrazine, indicating that its  $\theta$  value is even nearer the crossover point than the acyclic compound. The cis conformation can be ruled out because of the large  $\phi$  value required, as is  $T_2$  by the small size of the splitting. The pes splitting is only consistent with a  $T_1$  conformation having a rather larger  $\phi$  than those observed for the dialkylpyrazolidines. This seems quite reasonable since the ring methylene-*N*-alkyl substituent interaction which lowers  $\phi$  is substantially decreased. The qualitative result that  $T_1$  is preferred for both the diethyl and unsubstituted compounds, while  $T_2$  is preferred for dimethylpyrazolidine, was quite unexpected, and the steric arguments employed for **9-12** are clearly inadequate. A factor which could be important is that dipole-dipole interactions for the presumably comparatively polar N-H bonds would be expected to be lower for  $T_1$  than for  $T_2$ , but we cannot adequately explain the preference of **8** for the  $T_1$  conformation.

Turning to the bicyclic pyrazolidines **13-16**, the first surprise was that the major conformation of **14** has a splitting of about 0.64 eV higher than that of **13**, although the only difference in structure is insertion of methyls on the carbons  $\beta$  to the nitrogens. Since both **13** and **14** are known from nmr studies<sup>1b</sup> to be in cis fused conformations, the increase in  $\Delta$  observed must correspond to a decrease in  $\theta$ . Although  $\theta(\text{est})$  values in Table II show  $0^\circ$  for **14** and  $30^\circ$  for **13**, we must admit that the scaling of  $\Delta_{2.5}(\theta)$  working curve was influenced by this pair of compounds and that the errors near the extreme  $\theta(\text{est})$  values are likely to be the largest. We suggest that **13** is in the twisted conformation **13F**



( $\theta = \phi$  if the nitrogens are tetrahedral). Introduction of R = Me in **14** should destabilize conformation F because of the introduction of the approximately 1,3 eclipsed C-CH<sub>3</sub>-N-CH<sub>2</sub> interactions. We suggest that this results in a change of the stablest conformation of **14** to **14G**, in which the quaternary carbons are forced to become the flap carbons of 5-ring envelope conforma-

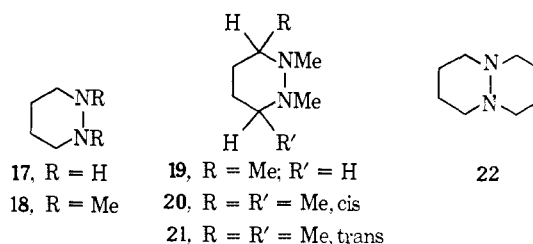
(11) For a discussion, see S. Wolfe, *Accounts Chem. Res.*, **5**, 102 (1972).

tions to reduce their nonbonded interactions. This forces  $\theta$  to assume a nearly  $0^\circ$  angle. From the  $IP_{\text{av}}$  values,<sup>4d</sup> it seems likely that both **13** and **14** are distorted from being tetrahedral at nitrogen, and that  $\theta(\text{est})$  values may be seriously off for this reason. We believe that there can be no question but that the major conformation of **14** has a substantially different  $\theta$  value than **13**, especially since a minor conformation, having a similar  $\theta$  value, was also observed.

Only a single conformation was observed for 1,6-diazabicyclo[4.3.0]nonane (**15**), and it showed a large splitting comparable to its homolog 1,6-diazabicyclo[4.4.0]decane (**22**), which is known to be trans fused from nmr studies.<sup>12</sup> A cis-fused **15** could only have a splitting this high if  $\theta$  were near  $0^\circ$ , which would be quite unreasonable structurally since this would require  $\phi \cong 0^\circ$  for the hexahydropyridazine ring.

Increasing the second ring in size by one more methylene group to give 1,7-diazabicyclo[5.3.0]decane (**16**) caused a substantial decrease in  $\theta$  for the major conformation and the appearance of a minor conformation. The  $\theta(\text{est})$  value of  $138^\circ$  for the major conformation is intermediate between these of the  $T_1$  and  $T_2$  conformations seen for the monocyclic compounds; the (CH<sub>2</sub>)<sub>5</sub> group is apparently not long enough to reach the low  $\Delta$  value seen for diethylpyrazolidine. Because  $IP_1$  from the minor conformers was obscured by that of the major conformer, we could not measure  $\Delta$  accurately. Although some cis-fused conformation does not seem structurally unlikely, we cannot justify such an assignment convincingly from the pes spectrum.

**3. Hexahydropyridazine Derivatives.** Seven hexahydropyridazine derivatives, **17-22**, were investigated



and the ionizations observed appear in Table III.

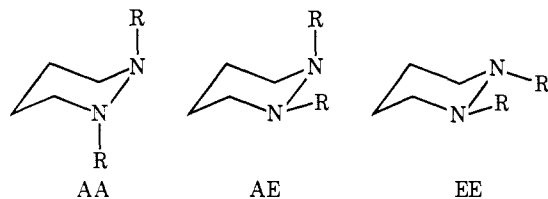
**Table III.** Photoelectron Spectral Data for Some Hexahydropyridazines

Compound	$IP_1$ , eV	$IP_2$ , eV	$\Delta$ , eV	$\theta(\text{est})$ , deg
<b>17</b>	8.64	9.49	0.85	
<b>18</b> (major)	7.81	10.13	2.32	164
<b>18</b> (minor)		8.85		
<b>19</b> (major)	7.83	8.78	0.95	51
<b>19</b> (minor)		9.99		
<b>20</b> (major)	7.76	8.68	0.92	53
<b>20</b> (minor)		9.72		
<b>21</b> (major)	7.82	8.66	0.84	55
<b>21</b> (trace)		9.74		
<b>22</b>	7.60	9.92	2.30	163

Three conformations are reasonable for a hexahydropyridazine, which ought to have axial or equatorial *N*-methyl substituents. Although the EE conforma-

(12) S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, **94**, 3138 (1972).

tion was initially assigned to 1,2-dimethylhexahydropyridazine (**18**) on the basis of nmr studies,<sup>1a</sup> later dipole moment work by Katritzky and coworkers<sup>1b</sup> showed that other conformations are certainly present, and they concluded from a combination of dipole moment and nmr spectral work on several derivatives that **18** exists as a 36:34:30 mixture of AA:AE:EE con-



formations at room temperature.<sup>13b</sup> Since the pes of hydrazines is mainly sensitive to  $\theta$ , one would expect to be able to distinguish the EE conformation, which ought to have large splitting, from the other two, but it is not clear that AA and AE would give different pes curves, since  $\theta \cong 60^\circ$  for both. The pes of **18** showed three lone pair ionization peaks, the ones of major intensity have a large  $\Delta$ , and a smaller intermediate peak, which we argue is associated with an  $IP_1$  peak which is obscured by  $IP_1$  of the major conformation.<sup>4</sup> The major conformer observed has such a large splitting that it can only correspond to EE; the similar splitting for **22**, which was indicated by nmr<sup>12</sup> to be trans fused and hence in the EE conformation, substantiates this. We assign the minor peak observed to AE and/or AA conformation. Since the EE conformation is only present in minor amounts for **19–21**, reasonably accurate  $\Delta$  values can be made for the AE/AA conformations giving  $\theta(\text{est})$  values of  $51\text{--}55^\circ$ . The high  $\theta(\text{est})$  solutions for the observed  $\theta$  values can be ruled out because they require an unreasonable amount of twist in the six-membered ring ( $\phi > 100^\circ$ ). If the AE conformation is the one being observed,  $\phi$  is near  $(120 - \theta)^\circ$ , or  $69\text{--}65^\circ$  for **19–21**. It would seem reasonable that  $\theta$  ought to be smaller than that estimated for an angle strain minimized hexahydropyridazine ring,<sup>14</sup> since the axial methyl-axial ring hydrogen interaction should decrease  $\theta$  and increase  $\phi$ . It must be admitted, however, that if the AA conformation were present, it could well have sufficiently distorted nitrogens to cause a larger splitting that  $\Delta_{2,3}(\theta)$  would predict, and it seems wise to conclude that AE and AA conformations would probably both contribute to the peaks observed.<sup>14a</sup>

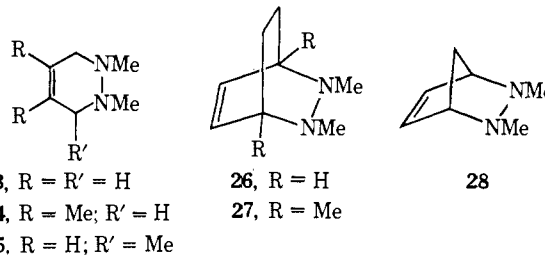
The decrease in importance of the EE conformation in **19–21** relative to **18** seems to demonstrate a reluctance for having equatorial methyl groups on three adjacent atoms.

(13) (a) R. A. Y. Jones, A. R. Katritzky, D. L. Ostercamp, K. A. F. Record, and A. C. Richards, *Chem. Commun.*, 644 (1971); (b) R. A. Y. Jones, A. R. Katritzky, D. C. Ostercamp, K. A. F. Record, and A. C. Richards, *J. Chem. Soc., Perkin Trans. 2*, 34 (1972).

(14) Using the conventional bond lengths (see footnote 10), the CCC bond angle depends only on the NNC bond angle. Assuming deformation of these angles to be equally costly in energy, one obtains  $\angle NCC = 110.8$  and  $\angle CCC = 108.1^\circ$ , leading to a  $C_6-N_1-N_2-C_3$  dihedral angle of  $62.1^\circ$  if  $\angle NCC$  is  $109.5^\circ$ . Jones, Katritzky, and coworkers<sup>13b</sup> used only a slightly different geometry. A standard Newman projection using  $\phi$  of  $60^\circ$  is a rather good approximation. The actual  $\phi$  value will, of course, depend upon nonbonded interactions which are not considered here.

(14a) NOTE ADDED IN PROOF. Recent low-temperature <sup>13</sup>C nmr studies have shown that only the EE and AE conformations of **18** are observable at low temperature, and that the EE conformation is the stablest: S. F. Nelsen and G. R. Weisman, *J. Amer. Chem. Soc.*, in press.

**4. 1,2,3,6-Tetrahydropyridazine Derivatives.** For these compounds, the olefin  $\pi$ -bond ionization comes near  $IP_2$  of the nitrogen lone pairs, complicating the lone pair region and making observation of peaks caused by minor isomers less likely. We observed single conformers for **23–28**. Since the  $\pi$  ionization for cyclo-



hexene occurs at  $9.12\text{ eV}$ <sup>15</sup> and the presence of the two  $\beta$  nitrogens is expected to increase  $IP(\pi)$  for **23**, the  $9.46\text{ eV}$  peak is reasonably assigned as  $IP(\pi)$ . This assignment was verified by the pes of **24**, for bis-methylation of the  $\pi$ -bond caused a substantial decrease in  $IP(\pi)$ , unfortunately causing it to overlap with  $IP_2(n)$ , causing more uncertainty than usual in the position of each level.

Although  $IP(\pi)$  for bicyclo[2.2.2]octene and bicyclo[2.2.1]heptene are  $0.07$  and  $0.15\text{ eV}$  lower than  $IP(\pi)$  of cyclohexene,<sup>15</sup> the assignments of Table IV<sup>16</sup> give  $\pi$

Table IV. Photoelectron Spectral Data for Some 1,2,3,6-Tetrahydropiperidazines

Compound	$IP_1(n)$ , <sup>a</sup> eV	$IP_2(n)$ , <sup>a</sup> eV	$IP(\pi)$ , <sup>b</sup> eV	$\Delta$ , <sup>c</sup> eV
<b>23</b>	8.12	8.86	9.46	0.74
<b>24</b>	7.92	$\sim 8.70$	$\sim 8.70$	$\sim 0.78$
<b>25</b>	8.08	8.78	9.37	0.70
<b>26</b>	7.49	9.49	9.15	2.00
<b>27</b>	7.43	9.47	9.01	2.04
<b>28</b>	7.72	9.63	9.25	1.91

<sup>a</sup> Ionization from orbitals assigned to (predominantly) lone pair. <sup>b</sup> Ionization from orbitals assigned to (predominantly) olefin. <sup>c</sup>  $IP_2(n) - IP_1(n)$ .

ionization lowerings of  $0.31$  and  $0.21$  for **26** and **28** compared with **23**, suggesting that some additional effect is being observed. An obvious candidate for the cause of this effect is  $n, \pi$  mixing. The amount of  $n, \pi$  mixing should be largest for the  $IP_2(n)$  lone pair combination orbital, both because it lies closer in energy and because the symmetry is correct; the nodal plane between the nitrogens in  $IP_1(n)$  will tend to largely cancel  $IP_1(n), \pi$  mixing. Interaction of  $IP_2(n)$  and  $IP(\pi)$  will raise the higher energy orbital and decrease the lower one, which would result in a decreased  $\Delta$  for **23–25** and an increased  $\Delta$  for **26–28** compared with a hypothetical saturated hydrazine of the same geometry. The size of this  $n-\pi$  mixing-induced change in  $\Delta$  will depend both upon the geometry of the system and on the (hypothetical) "unmixed"  $n$  and  $\pi$  energy levels. The observed data indicate that it is unwise to ignore the  $n-\pi$  mixing effect on  $\Delta$  for the bicyclic compounds. The best comparison is the observed  $\Delta$  for **2** ( $1.46$ ) and for **27** ( $2.04$ ).

(15) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969).

(16) These assignments differ from those suggested in the communication,<sup>4a</sup> which were corrected by Rademacher.<sup>5b</sup>

As discussed above, **2** is not torsionally twisted very much, and of course, **27** should be even less twisted, so  $\theta$  must be quite similar for these two compounds, yet  $\Delta$  differs by 0.58 eV. If the effects of  $n, \pi$  mixing on the spectra of **23** and **25** are ignored,  $\theta(\text{est})$  values of 59 and 60° are calculated, in agreement with the pseudo-equatorial-pseudoaxial *N*-methyl geometry assigned to them by Lambert.<sup>2a</sup> Particularly for **24**, we should have been able to observe  $\text{IP}_2(n)$  for the bis pseudo-equatorial conformation, had one been present in significant amount. The merging of  $\text{IP}_2(n)$  and  $\text{IP}(\pi)$  for **24** is a good argument that mixing of these levels is not large for monocyclic tetrahydropyridazines. "Through space" overlap of the  $n$  and  $\pi$  orbitals is much higher in the bicyclic compounds **26–28**.

**5. Relative Peak Sizes.** In several cases, we observed a third "lone pair" ionization for a hydrazine, and, as explained above, interpret this as being caused by the presence of more than one conformation. The pair of peaks from one conformation were frequently more intense than the observable ( $\text{IP}_2$ ) peak from the other conformation, so we have termed them "major" and "minor" conformations, respectively. It is tempting to try to relate the pes peak size to mole fraction of the conformations present. This wish is largely frustrated, both because of experimental difficulties in determining the size of the peaks (the peaks overlap badly) and because the cross sections for ionization of two different conformations would have to be identical for this to work quantitatively.

From the spectra of acyclic and 1,1-cycloalkylhydrazines, in which the complication of a second observed conformation is not present, it is clear that the pes peaks for the symmetric and antisymmetric lone pair combinations, which must be present in equal amounts, have different sizes. We have attempted to quantitate this difference in size by fitting the data with Gaussian curves, and comparing the half-widths and areas thus obtained (see Tables V–VII). There are

**Table V.** Acyclic Hydrazines. Half-Widths and Relative Areas of Gaussian Curves Fit to the Pes<sup>a</sup>

Compound	Half-width ( $\text{IP}_1$ ), eV	Area ( $\text{IP}_1$ ) <sup>b</sup>	Half-width ( $\text{IP}_2$ ), eV	Area ( $\text{IP}_2$ ) <sup>b</sup>
H <sub>2</sub> NNH <sub>2</sub>	0.69	0.67	1.02	1.00
MeHNNH <sub>2</sub>	0.81	1.00	0.72	0.63
EtHNNH <sub>2</sub>	0.78	1.00	0.67	0.57
<i>n</i> -A-HNNH <sub>2</sub>	0.76	1.00	0.60	0.50
<i>i</i> -PrHNNH <sub>2</sub>	0.70	1.00	0.79	0.96
<i>n</i> -BuHNNH <sub>2</sub>	0.78	1.00	0.61	0.47
<i>t</i> -BuHNNH <sub>2</sub>	0.72	1.00	0.80	0.83
Me <sub>2</sub> NNH <sub>2</sub>	0.69	1.00	0.74	0.77
<i>n</i> -Pr <sub>2</sub> NNH <sub>2</sub>	0.64	0.93	0.61	1.00
MeHNNHMe	0.60	0.70	0.88	1.00
<i>i</i> -PrHNNH- <i>i</i> -Pr	0.63	0.93	0.78	1.00
Me <sub>2</sub> NNHMe	0.67	1.00	0.62	0.88
Me <sub>2</sub> NNH- <i>i</i> -Pr	0.55	0.73	0.69	1.00
Me <sub>2</sub> NNMe <sub>2</sub>	0.53	0.82	0.58	1.00
Et <sub>2</sub> NNMe <sub>2</sub>	0.50	0.72	0.59	1.00
Et <sub>2</sub> NNEt <sub>2</sub>	0.46	0.52	0.62	1.00
Et <sub>2</sub> NN- <i>n</i> -Pr <sub>2</sub>	0.49	0.70	0.58	1.00
EtMeNNMe <sub>2</sub>	0.50	0.67	0.62	1.00
<i>n</i> -BuMeNNMe <sub>2</sub>	0.49	0.61	0.64	1.00
<i>i</i> -PrMeNNMe <sub>2</sub>	0.50	0.67	0.62	1.00
<i>i</i> -Pr <sub>2</sub> NNMe- <i>i</i> -Pr	0.51	0.83	0.63	1.00
<i>t</i> -BuMeNN- <i>t</i> -BuMe	0.45	0.56	0.79	1.00

<sup>a</sup> Best least-squares fit to data using Gaussian curves, by program GFIT. <sup>b</sup> Relative areas, larger set equal to 1.00.

**Table VI.** 1,1-Cycloalkylhydrazines. Half-Widths and Relative Areas of Gaussian Curves Fit to the Pes<sup>a</sup>

Compound	Half-width ( $\text{IP}_1$ ), eV	Area ( $\text{IP}_1$ ) <sup>b</sup>	Half-width ( $\text{IP}_2$ ), eV	Area ( $\text{IP}_2$ ) <sup>b</sup>
(CH <sub>2</sub> ) <sub>3</sub> NNH <sub>2</sub>	0.68	1.00	0.75	0.77
(CH <sub>2</sub> ) <sub>4</sub> NNH <sub>2</sub>	0.67	1.00	0.70	0.74
(CH <sub>2</sub> ) <sub>5</sub> NNH <sub>2</sub>	0.67	1.00	0.61	0.59
(CH <sub>2</sub> ) <sub>6</sub> NNMe <sub>2</sub>	0.59	1.00	0.57	0.97
(CH <sub>2</sub> ) <sub>4</sub> NN(CH <sub>2</sub> ) <sub>4</sub>	0.80	1.00	0.54	0.51
(CH <sub>2</sub> ) <sub>5</sub> NNMe <sub>2</sub>	0.50	0.65	0.62	1.00
(CH <sub>2</sub> ) <sub>5</sub> NN(CH <sub>2</sub> ) <sub>4</sub>	0.56	0.95	0.54	1.00
(CH <sub>2</sub> ) <sub>7</sub> NN(CH <sub>2</sub> ) <sub>5</sub>	0.44	0.37	0.73	1.00

<sup>a</sup> Best least-squares fit to the data using Gaussian curves, by program GFIT. <sup>b</sup> Relative areas, larger set equal to 1.00.

regular trends in whether  $\text{IP}_1$  or  $\text{IP}_2$  is largest as the structure is altered, suggesting that the numbers thus generated have some significance. For the acyclic hydrazines,  $\text{IP}_1$  is largest for the six monoalkyl compounds studied, but  $\text{IP}_2$  is largest for the nine tetraalkylhydrazines. The smaller peak was 58–80% as large in area as the larger one for these compounds. The possibility that  $\theta$  is on different sides of the crossover point (where  $n_+$  and  $n_-$  have the same energy) and hence that the larger peak in all cases is the  $n_+$  combination (hydrazine itself has  $n_+$  largest, since  $\theta$  is 90–95°, this makes  $n_-$  correspond to  $\text{IP}_1$ ) cannot be proven from our data. It will be noted that quite large half-widths are observed for hydrazine lone pair ionizations, generally 0.5–1 eV. One factor which we believe should contribute to the peak width is that  $\Delta$  is sensitive to  $\theta$ , and that the energy minimum is fairly broad, so that the spectrum observed should in fact be the weighted summation of spectra for a range of  $\theta$  values near enough the  $\theta$  of minimum energy to be thermally populated.

When more than one conformation is observed, one must consider that even if two conformations were actually present in equal amount, their  $\text{IP}_2$  peak sizes would be expected to differ by up to a factor of 2. Nevertheless, we wish to point out that the relative amounts of the two superimposed spectra observed for hexahydropyridazine (**17**) are rather surprising. The observed area for  $\text{IP}_2$  of the "minor" conformation, which may be confidently assigned to **17AE** + **17AA**, is only one-third the size of  $\text{IP}_2$  for **17EE**. This may be contrasted with the result of Katritzky and coworkers,<sup>13</sup> who determined that **17AE** + **17AA**/**17EE** is two, using a combination of dipole moment and nmr studies on models. Further work will be required to find out why the pes result appears to disagree qualitatively with the solution work. Several possibilities, including a far higher cross section for ionization of **17EE** than for the other conformations, are present.<sup>14a</sup>

## Conclusion

The pes of 1,2-cycloalkylhydrazines gives conformational information which is not readily obtainable by other techniques. By using a semiempirical curve, the lone pair-lone pair dihedral angle  $\theta$  is easily obtained, and from this such detailed information as the direction and amount of torsion in bicyclo[2.2.2] and pyrazolidine rings can be obtained. Several compounds showed evidence for two or more conformations of similar enough energy for them to be populated at room temperature. Because of the lack of structural determina-

Table VII. 1,2-Cycloalkylhydrazines. Half-Widths and Relative Areas of Gaussian Curves Fit to the Pes<sup>a</sup>

Compound	Half-width (IP <sub>1</sub> ), eV	Area (IP <sub>1</sub> ) <sup>b</sup>	Half-width (IP <sub>2</sub> ), eV	Area (IP <sub>2</sub> ) <sup>b</sup>	Half-width (IP(n)) <sup>c</sup>	Area (IP(n)) <sup>b, c</sup>
1	0.65	0.55	1.13	1.00 <sup>d</sup>		
2	0.62	0.82	0.74	1.00		
3	0.73	0.64	0.65	1.00	0.59	0.2
4	0.55	0.64	0.81	1.00		
5	0.65	0.51	0.47	1.00		
6	0.65	0.75	0.65	1.00		
7	0.61	0.65	0.69	1.00		
8	0.76	1.00	0.62	0.70		
9	1.07	1.00	0.54	0.41	1.12	0.61
10	0.75	0.85	0.80	1.00		
11	0.76	0.77	0.81	1.00		
14	0.74	0.93	0.59	1.00	0.23	0.07
15	0.74	0.76	0.56	1.00		
16	0.56	1.00	0.59	0.90		
17	0.76	1.00	0.65	0.90		
18	0.78	1.00	0.55	0.86	0.54	0.28
19	0.56	0.96	0.55	1.00	0.32	0.06
20	0.60	0.94	0.50	1.00	0.03	<0.01
21	0.51	0.74	0.58	1.00	0.07	0.01

<sup>a</sup> Best least-squares fit to data using Gaussian curves, by program GFIT. <sup>b</sup> Relative areas, larger set equal to 1.00. <sup>c</sup> For IP<sub>2</sub> of minor conformation, IP<sub>1</sub>'s quoted in the second column, includes both conformations. <sup>d</sup> IP<sub>2</sub> badly overlapping with  $\sigma$  ionizations. Area inaccurate.

tions, the  $\theta$  values obtained from pes could only be tested by internal comparisons but appear to be reasonable on steric grounds. Deviations appear to result for (strained) conformations which result in large  $\Delta$  values. It is suggested that 2,3-diazabicyclo[2.2.1]heptane derivatives are too strained to allow use of the same curve to obtain reasonably accurate  $\theta$  values as is used for less strained compounds. Bicyclic tetrahydropyrazidines have large enough  $n, \pi$  interactions to change the size of  $\Delta$  significantly.

The presence of detectable amounts of more than one conformation suggested by pes for some compounds is presently being investigated in these laboratories by other techniques, both to verify their presence and to evaluate how successful estimation of relative amounts of conformational mixtures by use of pes will be.

### Experimental Section

The preparation and properties of most of the compounds employed have been previously described: **1**, **3**, **6**, **9–11**, **13**, **17–26**, **28**;<sup>17</sup> **15** and **16**;<sup>18</sup> **7**;<sup>19</sup> **4** and **5**;<sup>20</sup> **8**;<sup>21</sup> **14**.<sup>22</sup> Compounds **2** and **27** were prepared by lithium aluminum hydride reduction<sup>1a</sup> of the corresponding biscarbamates<sup>23</sup> and had the expected spectral properties and empirical formulas.

**4,4-Diethyl-1,2-dimethylpyrazolidine (12).** A mixture of 200 ml of dry tetrahydrofuran and 3.3 g of lithium aluminum hydride was refluxed over 5.5 g of 4,4-diethylpyrazolidine-3,5-dione<sup>24</sup> contained

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(19) S. F. Nelsen and R. T. Landis, II, *J. Amer. Chem. Soc.*, **95**, 5422 (1973).

(20) E. E. Mikhlina, N. A. Kamarova, and A. V. Rubstov, *Chem. Abstr.*, **65**, 717a (1966).

(21) E. C. Buhle, A. M. Moore, and F. Y. Wiseogle, *J. Amer. Chem. Soc.*, **65**, 29 (1943).

(22) S. F. Nelsen, G. R. Weisman, P. J. Hintz, D. Olp, and M. R. Fahey, *J. Amer. Chem. Soc.*, **96**, 2916 (1974).

(23) We thank Professor P. Engel for providing experimental detail for preparation of the biscarbamates prior to publication.

(24) H. Stetter and P. Woernle, *Justus Liebigs Ann. Chem.*, **724**, 150 (1969).

in a Soxhlet extractor for 30 hr, excess hydride was destroyed by addition of water and 15% sodium hydroxide, and the filtrant was fractionally distilled, giving 1.5 g of a mixture of products, bp (15 mm) 82–88°. To 15 ml of acetonitrile, 2 ml of formalin, and 800 mg of sodium cyanoborohydride, 640 mg of the above mixture was added, followed by 20 drops of acetic acid added in five-drop batches over a 4-hr period.<sup>18</sup> After stirring at room temperature for 15 hr, extraction with four 25-ml portions of pentane followed by concentration gave a yellow oil with an odor like camphor. The **12** formed was isolated by vapor phase chromatography on an XF-1150 column; **12** was the first peak observed beyond the solvent peak and obtained as a colorless oil. Spectral properties: nmr (CDCl<sub>3</sub>)  $\delta$  2.57 (s, 4 H), 2.44 (s, 6 H), 1.50 (quartet showing second-order splittings, 4 H), 0.83 (triplet showing second-order splittings, 6 H); ir (CDCl<sub>3</sub>) no NH or CO absorption; empirical formula C<sub>9</sub>H<sub>20</sub>N by high resolution mass spectral analysis (calculated, 156.1625, observed 156.158).

**Photoelectron Spectra.** All compounds were purified by vapor phase chromatography (10 ft, 15% XF 1150 on Chromosorb W column, Aerograph 90 P.3 instrument) before use and run at room temperature. A Varian IEE.15 instrument was used with a Helium I arc. Typically a 10-V scan from 16.5 to 6.5 eV was determined to locate the peaks, and the lone pair and argon regions were scanned separately at 1–3 eV scan widths, time averaging over 40 30-sec scans, to collect the data used for determination of accurate peak positions. It was found that simply visually identifying the peak maxima from an  $x, y$  plot of the data (as was done for the numbers quoted in the communications<sup>4a, b</sup>) introduced significant error, when compared with the contents of the data channels. The peak positions and intensities quoted were all determined by fitting the data with Gaussian curves, using program GFIT,<sup>4c</sup> written by Dennis Lichtenberger, University of Wisconsin. All ionizations quoted use the 15.759-eV argon line, added as an internal standard, for determination of ionization potential. Photographs of all of the 10 eV wide spectra appear in the thesis.<sup>25</sup>

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(25) J. M. Buschek, Thesis, University of Wisconsin, 1973.