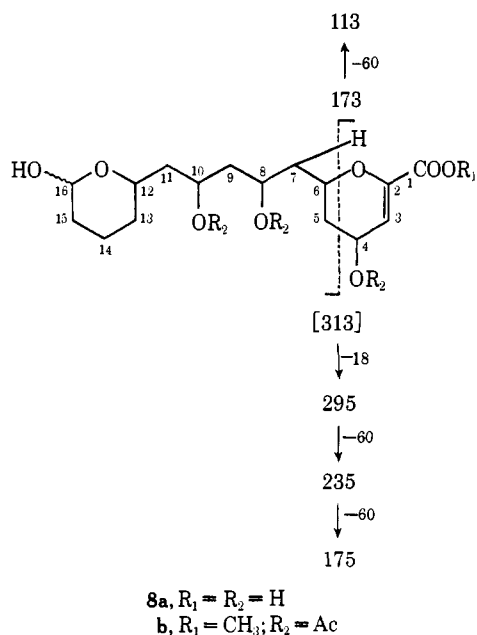


means of the mass spectrum,<sup>4</sup> in which the most intense peaks correspond to pyrylium ( $m/e$  81) and dihydropyrylium ( $m/e$  83) ions.

Finally, treatment of **1** with NaIO<sub>4</sub> gave an acidic compound, **8a**, which, on treatment with CH<sub>2</sub>N<sub>2</sub> and



Ac<sub>2</sub>O, in that order, afforded **8b** ( $m/e$  468,  $M - \text{H}_2\text{O}$ ),<sup>4</sup> showing uv absorption at 224 nm and, in the pmr spectrum (CDCl<sub>3</sub>), one olefinic proton ( $\delta$  6.03), three CHOAc groups, and a free anomeric proton absorbing in the range  $\delta$  5.3–4.7 derived from partial deacetylation during isolation.<sup>5</sup> Compound **8a** would originate from the cleavage of bonds C-15–C-16 and C-31–C-32, followed by decarboxylation of an  $\alpha,\beta$ -diketo acid intermediate, oxidation at C-16, cyclization, and loss of an H<sub>2</sub>O molecule from the resulting  $\alpha$ -keto acid.

The above data require the axenolide be represented as **1**; the lactone ring formed by the carboxyl at C-16 (for which no data on the determination of the size are presently available) is supposed to be a six-membered ring.

(4) The masses of the principal fragment ions of the seco compounds were determined by high resolution mass spectrometry and agreed with the calculated values within acceptable limits. In the formulas the most significant ions are indicated.

(5) An acetylation experiment performed in the pmr tube (C<sub>6</sub>D<sub>6</sub>N) showed a shift to lower field of one proton.

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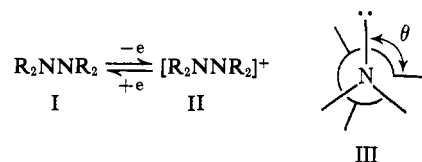
### Photoelectron Spectra of Hydrazines. I. Dependence of the Lone Pair–Lone Pair Splitting on Dihedral Angle for Tetraalkylhydrazines

Sir:

We have been particularly interested in the molecular geometry of hydrazines in conjunction with studies of the tetraalkylhydrazine (I)–hydrazinium radical cation (II) redox couple,<sup>1</sup> which have shown a substantial sensitivity of  $E_{1/2}$  to structure. *Ab initio* calculations

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

on hydrazine<sup>2</sup> and methylhydrazine<sup>2f</sup> indicate that the lone pair–lone pair dihedral angle  $\theta$  (see III) is about 90°



in agreement with far-infrared<sup>3a</sup> and microwave<sup>3b–d</sup> results. It has been widely accepted that this is largely a result of repulsion between the four lone pair electrons in two adjacent orbitals;<sup>2</sup> their overlap is minimized at  $\theta = 90^\circ$ .<sup>4</sup>

In more complex molecules, steric effects can clearly alter  $\theta$ , as nmr studies of cyclic tetraalkylhydrazines<sup>5</sup> and bis(hydrazines)<sup>6</sup> have shown.

We report here the photoelectron spectra<sup>7</sup> (pes) of several tetraalkylhydrazines, which demonstrate that pes show a substantial dependence upon  $\theta$ . The pes for **1–9** had broad peaks which were usually well resolved from the continuum absorption caused by  $\sigma$ -bond ionization. Two such peaks were observed for all but **3**, **4**, and **7**, in which olefinic or oxygen lone pair ionizations result in low energy peaks (see Figure 1). From pes studies of amines<sup>8</sup> and other hydrazines,<sup>9</sup> ionization from the “lone pair” orbitals is expected to occur at lower energy than those from the  $\sigma$  bonds, and we have assigned the lowest energy ionizations, which occur below 10.5 eV, to the “lone pair” ionizations. Our data<sup>10</sup> are summarized in Table I.

Two “lone pair” ionizations are expected for a hydrazine group, corresponding to the symmetric ( $n_+$ ) and antisymmetric ( $n_-$ ) combinations of the “lone pair” orbitals. Substantial variation in the size of the difference of these ionization potentials (designated  $\Delta$  in Table I) was observed with structure, and a dominant inductive effect is ruled out by the data. Included in Table I are estimates for  $\theta$ , derived from nmr studies.<sup>5,6</sup>

**1** exists in the anti conformation **1a<sup>bb</sup>** ( $\theta$  about 180°), while **5** is in a syn conformation (**5a**), presumably twisted somewhat from  $\theta = 0$  by both steric and electronic interactions. **2–4** are in approximately eclipsed ( $\theta = 120^\circ$ ) conformations like **2a**, which may well deform slightly to increase the methyl–methyl distance and lower  $\theta$ , whereas **6** and **7** are more flexible, and should be able to more closely approach the electronically

(2) (a) A. Veillard, *Theor. Chim. Acta*, **5**, 413 (1966); (b) W. H. Fink, D. C. Pan, and L. C. Allen, *J. Chem. Phys.*, **47**, 895 (1967); (c) L. Pedersen and K. Morokuma, *ibid.*, **46**, 3941 (1967); (d) H. Yumabe, H. Kato, and T. Yonezawa, *Bull. Soc. Chem. Jap.*, **44**, 22 (1971); (e) E. L. Wagner, *Theor. Chim. Acta*, **23**, 115 (1971); (f) L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **94**, 2371 (1972).

(3) (a) T. Kasuya, *Sci. Pap. Inst. Phys. Chem. Res., Tokyo*, **56**, 1 (1962); (b) A. Yamaguchi, I. Ichisima, T. Shimanovchi, and S. Mizushima, *Spectrochim. Acta*, **16**, 1471 (1960); (c) R. P. Lattimer and M. D. Harmony, *J. Chem. Phys.*, **53**, 4775 (1970); (d) R. P. Lattimer and M. D. Harmony, *J. Amer. Chem. Soc.*, **94**, 351 (1972).

(4) Recently, Radom, Hehre, and Pople<sup>2f</sup> have suggested that “back-bonding” between the N–H bonds and the lone pair orbitals, which is maximized at  $\theta = 90^\circ$ , is responsible.

(5) (a) J. P. Klintzinger, J. M. Lehn, and J. Wagner, *Chem. Commun.*, 206 (1967); (b) J. E. Anderson, *J. Amer. Chem. Soc.*, **91**, 6374 (1969), and references therein.

(6) (a) J. E. Anderson and J. D. Roberts, *ibid.*, **90**, 4186 (1968); (b) S. F. Nelsen and P. J. Hintz, *ibid.*, **94**, 3138 (1972).

(7) For a review, see S. D. Worley, *Chem. Rev.*, **71**, 295 (1971).

(8) D. W. Turner, *Advan. Phys. Org. Chem.*, **4**, 31 (1966).

(9) N. Bodor, M. J. S. Dewar, W. B. Jennings, and S. D. Worley, *Tetrahedron*, **26**, 4109 (1967).

(10) Determined on a Varian IEE-15 instrument.

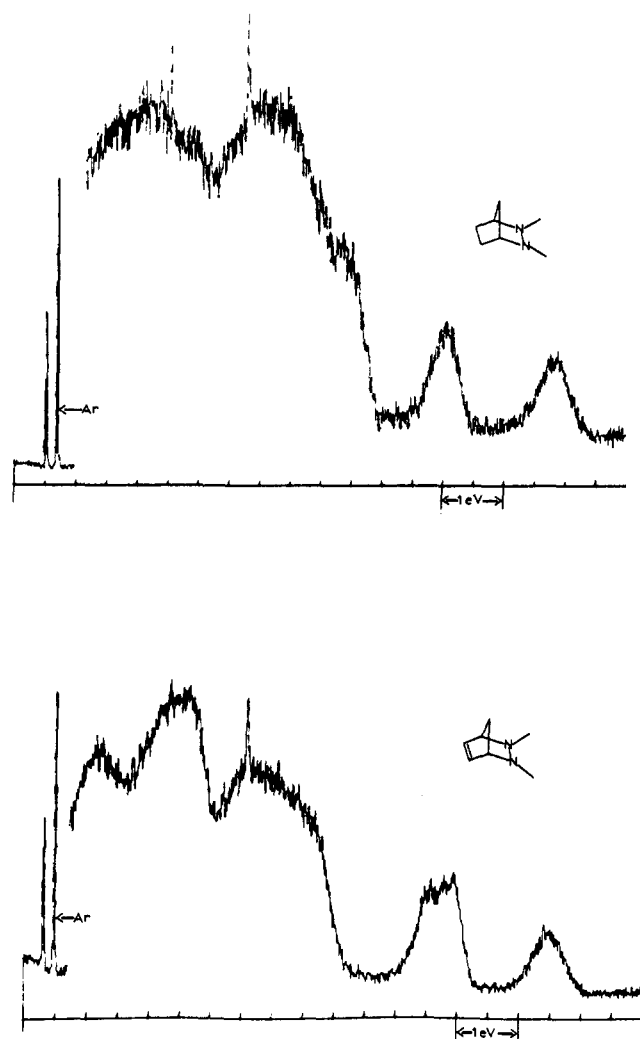
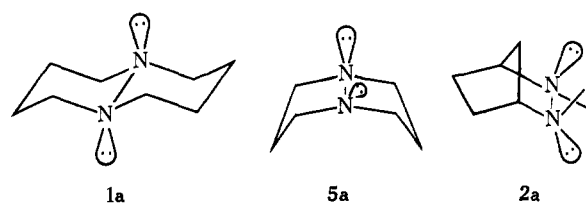


Figure 1. Sample photoelectron spectra for 2 and 3.



preferred  $\theta = 90^\circ$ . The acyclic tetraalkylhydrazines **8** and **9** can presumably most closely approach  $\theta = 90^\circ$ .

From Table I, we believe it is clear that the interaction between the two lone pair orbitals on nitrogen, which should vary (to a first approximation) as their overlap,<sup>11</sup> is an important contribution to the observed  $\Delta$ . Using  $sp^3$  hybridized Slater ao's on nitrogen at 1.45 Å, nearly a  $\cos \theta$  relationship is observed for the overlap of both  $n_+$  and  $n_-$ , resulting in nearly equal overlaps at  $\theta = 0$  and  $180^\circ$  and nearly zero overlap at  $90^\circ$ ; the curves are much like those shown by Hoffmann<sup>11</sup> for  $sp^2$  hybrids on carbon. Calculated lone pair-lone pair splittings for hydrazine were 2.33 eV for  $\theta = 0^\circ$ , 0.22 for  $\theta = 90^\circ$ ,<sup>2d</sup> 0.31 for *trans*-diaziridine, and 0.69 for *cis*-diaziridine.<sup>12</sup> Our experimental results parallel this behavior in that the splittings are largest for **1**, intermediate for the other bicyclic com-

(11) R. Hoffmann, *Accounts Chem. Res.*, 4, 1 (1971).

(12) J. P. Snyder, *Tetrahedron Lett.*, 2451 (1972).

Table I. Pes Ionization Potentials for Hydrazines

Compound	No.	$I_{p1},^a$ eV	$I_{p2},^a$ eV	Other ( $<10.5$ eV)	$\Delta$	Estd $\theta$ , deg
	1	7.59	10.04		2.45	180
	2	7.58	9.39		1.81	$\leq 120$
	3	7.59	9.29	9.56 <sup>b</sup>	1.71	$\leq 120$
	4	7.74	9.29	9.65 <sup>b</sup>	1.55	$\leq 120$
	5	7.91	9.43		1.52	10–30
	6	7.89	8.77		0.88	ca. 100?
	7	8.15	8.99	9.77 <sup>c</sup>	0.78	ca. 100?
$\text{Et}_2\text{NNEt}_2$	8	8.10	8.50		0.40	ca. 90
$\text{Me}_2\text{NNMe}_2$	9	8.43	8.83		0.40	ca. 90

<sup>a</sup> Calibrated to the 15.759-eV argon line. <sup>b</sup> Assigned to the olefin. <sup>c</sup> Assigned to an oxygen lone pair.

pounds, and smallest for the acyclic hydrazines, which have  $\theta$  close to  $90^\circ$ . The splitting does not go to zero at  $90^\circ$ , however. Other factors are clearly involved in determining the splitting. Mixing of the "lone pair" orbitals with the CN bonds  $\alpha$  to the nitrogen, the N–N bond, CN bonds  $\beta$  to the nitrogen, and other  $\sigma$  bonds at longer range are probably all involved to some extent. The former two are independent of  $\theta$ , and may well cause the 0.4 eV residual splitting at  $\theta = 90^\circ$ . Both the  $n_+$  and  $n_-$  "lone pair" orbitals are comparably broadened, indicating mixing with other orbitals for both; it is with good reason we write "lone pair" in quotation marks.

Although both electrolytic oxidation and pes formally concern the reaction  $\text{I} \rightarrow \text{II}$  and yield oxidation potentials in eV, there is little correlation between  $E_{1/2}$  and  $I_{p1}$  for these hydrazines. For example,  $E_{1/2}$  for **1** is 220 meV more anodic ("higher") than for **5**, but  $I_{p1}$  of **1** occurs at 320 meV lower energy than **5**. A fairly good linear correlation of  $E_{1/2}$  and vertical ionization potential (either from pes peak potentials or mass spectrum appearance potentials) has been found for a wide variety of compounds,<sup>13</sup> but such a trend clearly does not exist for tetraalkylhydrazines. We suggest that this is largely a result of the great difference in time scale for the electrolytic and pes oxidation experiments and that the hydrazinium cation formed in the pes experiment does not have time to undergo the conformational changes frequently necessary for reaching the most favorable geometry of the hydrazinium cation. The electrolytic  $E_{1/2}$  measures the potential at which electron transfer from neutral hydrazine and to equilibrated hydrazinium cation have the same rate. The geometry

(13) L. L. Miller, G. D. Nordblom, and E. A. Mayeda, *J. Org. Chem.*, 37, 916 (1972).

of hydrazine and equilibrated hydrazinium cation are very different.<sup>14</sup> 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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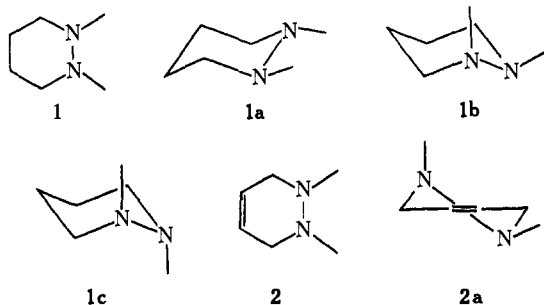
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## Photoelectron Spectra of Hydrazines. II. Conformations of Hexahydropyridazines

Sir:

The conformations of six-ring hydrazines are still in dispute. Anderson<sup>1</sup> 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  $-120^\circ$  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<sup>2</sup> disputed these interpretations.

They noted that the nmr spectrum of **1** could be a mixture of **1a**, **1b**, and **1c** if they interconvert at  $-120^\circ$ , 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,<sup>2b</sup> 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  $-90^\circ$ , 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.

Since **1a** has an antihydrazine configuration ( $\theta \sim$

(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).

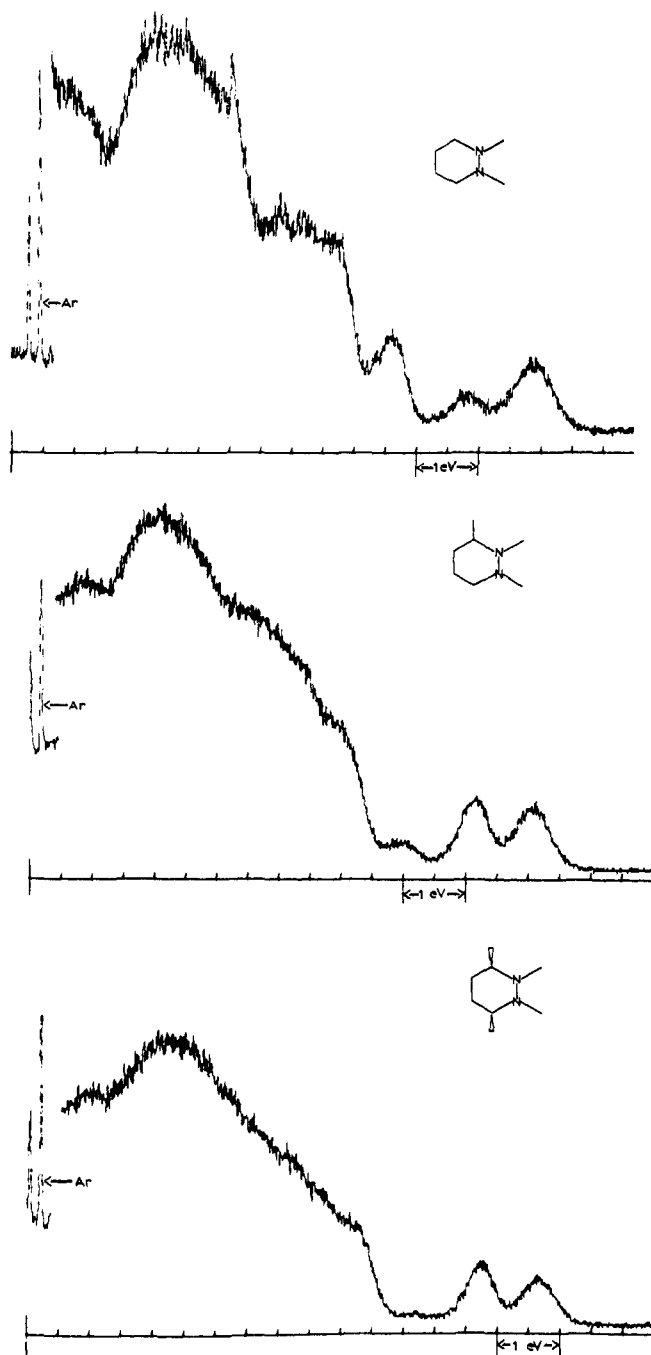


Figure 1. Photoelectron spectra of **1**, **5**, and **4**, illustrating the variation in the relative intensities of  $I_{p2}$  and  $I_{p3}$ .

$180^\circ$ ), its lone pair-lone pair splitting should be quite large compared to those of **1b** and **1c** ( $\theta \sim 60^\circ$ ) 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.<sup>3</sup> 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 ( $\Delta = 2.31$ ) in the vapor phase at room temperature, with **1b** and/or

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