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PHOTOELECTRON SPECTRA AND CONFORMATION OF CYCLIC N,N'-DIMETHYLHYDRAZINES

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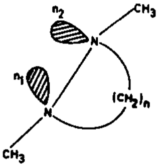
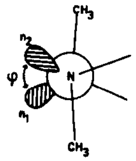
The conformation of symmetric hydrazines RR'N-NRR' can be determined by photoelectron (PE) spectroscopy.[1-3] Assuming that the interaction between the electron lone-pairs n_1 and n_2 is determined mainly by the dihedral angle φ, the angular dependence of the splitting between the two molecular orbitals $n_+=(n_1+n_2)/\sqrt{2}$ and $n_-=(n_1-n_2)/\sqrt{2}$ can be expressed by a function of the type

$$\Delta E = E(n_-) - E(n_+) = A \cos\varphi + B.$$

The results obtained previously[3] lead to the following values of the coefficients: $A=2.17$ eV and $B=-0.35$ eV.





In order to find out how sensitive this method is towards small changes of φ, it has been applied to the cyclic N,N'-dimethylhydrazines <u>1</u> to <u>10</u>.

The PE-spectra[4] of <u>1</u> to <u>6</u> from 6.0 to 12.0 eV, where the ionization potentials of n_+ and n_- are to be expected, are shown in figure 1. The bands of the π-electrons of the unsaturated compounds <u>5</u>, <u>8</u>, and <u>10</u>, which are also situated in this region, are easily identified in analogy to corresponding hydrocarbons.5) Using Koopmans theorem6) the orbital energies $E(n_+)$ and $E(n_-)$ are obtained from the spectra as the negative values of the vertical ionization potentials I_v. The data for the compounds 1 to 10 are collected in the following table.

Compound	$I_v(n_+)$ (eV)	$I_v(n_-)$ (eV)	$I_v(\pi)$ (eV)	ΔE (eV)	φ (°)
1,2-Dimethyldiaziridine (1)7)	9.42	11.44		-2.02	140
1,2-Dimethyldiazetidine (2)	7.95	10.07		-2.12	145
1,2-Dimethylpyrazolidine (3)	7.90	10.12		-2.22	150
	9.05	8.35*)		0.70	61
1,2-Dimethylpiperidazine (4)8)	7.78	10.10		-2.32	155
	8.57	7.9*)		0.67	62
1,2-Dimethyl-1,2,3,6-tetrahydropyridazine (5)	8.89	8.13	9.47	0.76	59
1,2,4,5-Tetramethylhexahydro-1,2,4,5-tetrazine (6)	7.90	10.37		-2.47	168
	9.00	8.45		0.55	65
2,3-Diaza-2,3-dimethylbicyclo[2.2.1]heptane (7)9)	7.48	9.30		-1.82	133
2,3-Diaza-2,3-dimethylbicyclo[2.2.1]heptene-(5) (8)9)	7.63	9.55	9.22	-1.92	136
2,3-Diaza-2,3-dimethylbicyclo[2.2.2]octane (9)	7.45	9.18		-1.73	130
2,3-Diaza-2,3-dimethylbicyclo[2.2.2]octene-(5) (10)9)	7.51	9.52	9.30	-2.01	140

*) shoulder

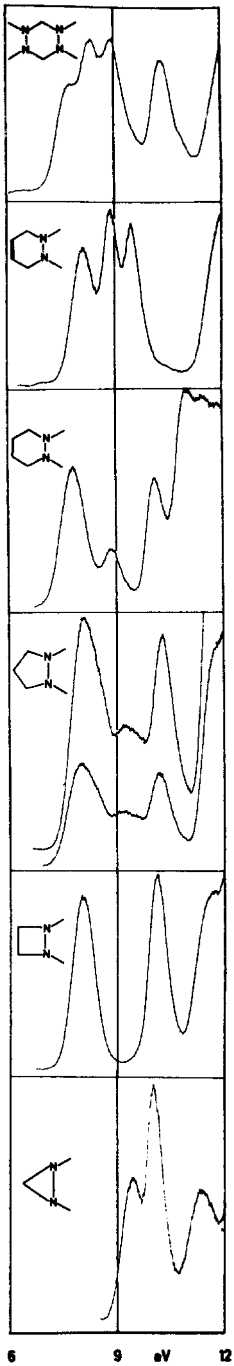


FIGURE 1.

In the series 1 to 4 φ increases significantly due to greater flexibility of the ring system. For 3 and 4 a dominant conformation with $\varphi = 150^\circ$ or 155° respectively and a second conformation with $\varphi \approx 60^\circ$ are observed. The methyl groups of 3 and 4 are therefore diequatorial in the more stable conformation and diaxial in the other one.9) The six membered ring of 5 is fixed in a conformation with one axial and one equatorial methyl group as was also shown by NMR measurements.10)

On the basis of calculated conformational energies and dipole moments it was predicted that the predominant conformation of 6 possesses one pair of diaxial and one pair of diequatorial **vicinal** methyl groups.11) This prediction is verified by the PE-spectrum of 6: Assigning the bands at 7.9 and 10.37 eV to the diequatorial and the bands at 8.45 and 9.00 eV to the diaxial dimethylhydrazine fragment respectively, dihedral angles of 168° and 65° are obtained.

In accordance with NMR results12) it is found that in the bicyclic compounds 7 to 10 n_1 and n_2 as well as the methyl groups are in trans positions. The substitution of the methylene by an ethylene bridge does not lead to a significant change of φ. But the data suggest that for the unsaturated compounds 8 and 10 φ is slightly larger than for the corresponding saturated compounds 7 and 9. However, this might be due as well to a small interaction between n_- and the π-orbital leading to a stabilisation of n_- and thus to an increased split of n_+ and n_-.

The results for the compounds 1 to 10 demonstrate the high advantage of PE spectroscopy for the conformational analysis of hydrazine derivatives. Contrary to studies on other compounds[13] they lead to the conclusion that the splitting between n_+ and n_- is due predominantly to a direct interaction of n_1 and n_2 and that interactions with other orbitals have a minor effect.

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8.) Compare 2.)

9.) Compare 1.)

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12.) J.E.Anderson and J.M.Lehn, *J.Amer.Chem.Soc.* **89**, 81 (1967).

13.) Compare e.g.: E.Haselbach, E.Heilbronner, A.Mannschreck, and W.Seitz, *Angew.Chem.* **82**, 879 (1970); *Angew.Chem.Int.Edn.* **9**, 901 (1970); H.Bock and B.G.Ramsey, *Angew.Chem.* **85**, 773 (1973).