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PHOTOELECTRON SPECTRA AND CONFORMATIONS OF TETRAHYDRO-1,2-OXAZINES AND ISOXAZOLIDINES

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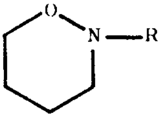
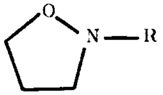
Photoelectron Spectroscopy (PES) has proved useful as an efficient experimental tool for conformational analysis of molecules possessing vicinal electron lone-pairs.[2] Theoretical studies on hydroxylamine (1)[3] and its methyl derivatives (2)[4,5] indicate that the split of the two highest occupied molecular orbitals (n_N and n_O) varies suffiently with the torsional angle φ = $\angle$:N-O-R to make different conformers distinguishable by PES.

In cyclic compounds φ depends on the ring size and the position of the nitrogen substituent R. In tetrahydro-1,2-oxazines φ is $\approx 60^\circ$ for equatorial (e) R and $\approx 180^\circ$ for axial (a) R. The corresponding values for isoxazolidines are estimated to be $50 - 70^\circ$ (e) and $150 - 180^\circ$ (a) depending on the puckering of the five membered ring. Besides different energies of R in e- or a-positions the value of the torsional potential of the N-O-bond contributes to the relative stabilities of different conformers.[6]

We have investigated the tetrahydro-1,2-oxazines 3 - 5 and the isoxazolidines 6 - 8. The lone-pair ionization potentials[7] are listed in the Table.

While the spectra of the six-ring compounds 3 - 5 show only two bands in the lone-pair ionization region (8 - 11 eV) with nearly the same splitting (1.25 - 1.45 eV) corresponding to e-conformers, two pairs of bands are present in the five-ring compounds 6 - 8 indicating mixtures of two different conformers. The relative intensities of the bands change with temperature and with the size of R. In the spectra of 7 and 8 the dominant pair with $\Delta I_v \approx 2$ eV corresponds to e-forms. In 6 the intense bands are split by only 0.84 eV indicating a dominant a-form.

Table : Vertical Ionization Potentials (eV) of 3 - 8

	R		$I_v(n_N)$	$I_v(n_O)$	ΔI_v	Position of R
	H	3	9.00	10.25	1.25	e
	CH_3	4	8.66	10.11	1.45	e
	$C(CH_3)_3$	5	8.27	9.70	1.43	e
	H	6	9.57 9.2 sh	10.41 11.0 sh	0.84 1.8	a e
	CH_3	7	8.60 9.1 sh	10.65 10.2 sh	2.05 1.1	e a
	$C(CH_3)_3$	8	8.25 8.7 sh	10.40 9.9 sh	2.15 1.2	e a

sh = shoulder

In the isoxazolidine series 6 - 8 the substitution of the nitrogen H-atom by an alkyl group is accompanied by a change of the favoured conformation from a to e. From the relative intensities of the pairs of bands at 20° C the conformer ratio e : a is calculated to be 1 : 3, 4 : 1, and 10 : 1 for 6, 7, and 8 respectively.

These findings are confirmed by force field calculations[5] using the results of an ab initio investigation[8] for the N-O torsional potential. For 3 and 4 chair conformations with equatorial substituents were found to be clearly favoured over other conformations. Contrarily the calculated energies of e- and a-forms of 6 and 7 differ only slightly.

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References and Notes

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