

PHOTOELECTRON SPECTRA OF CYCLOPENTANONE AND CYCLOHEXANONE ENAMINES.

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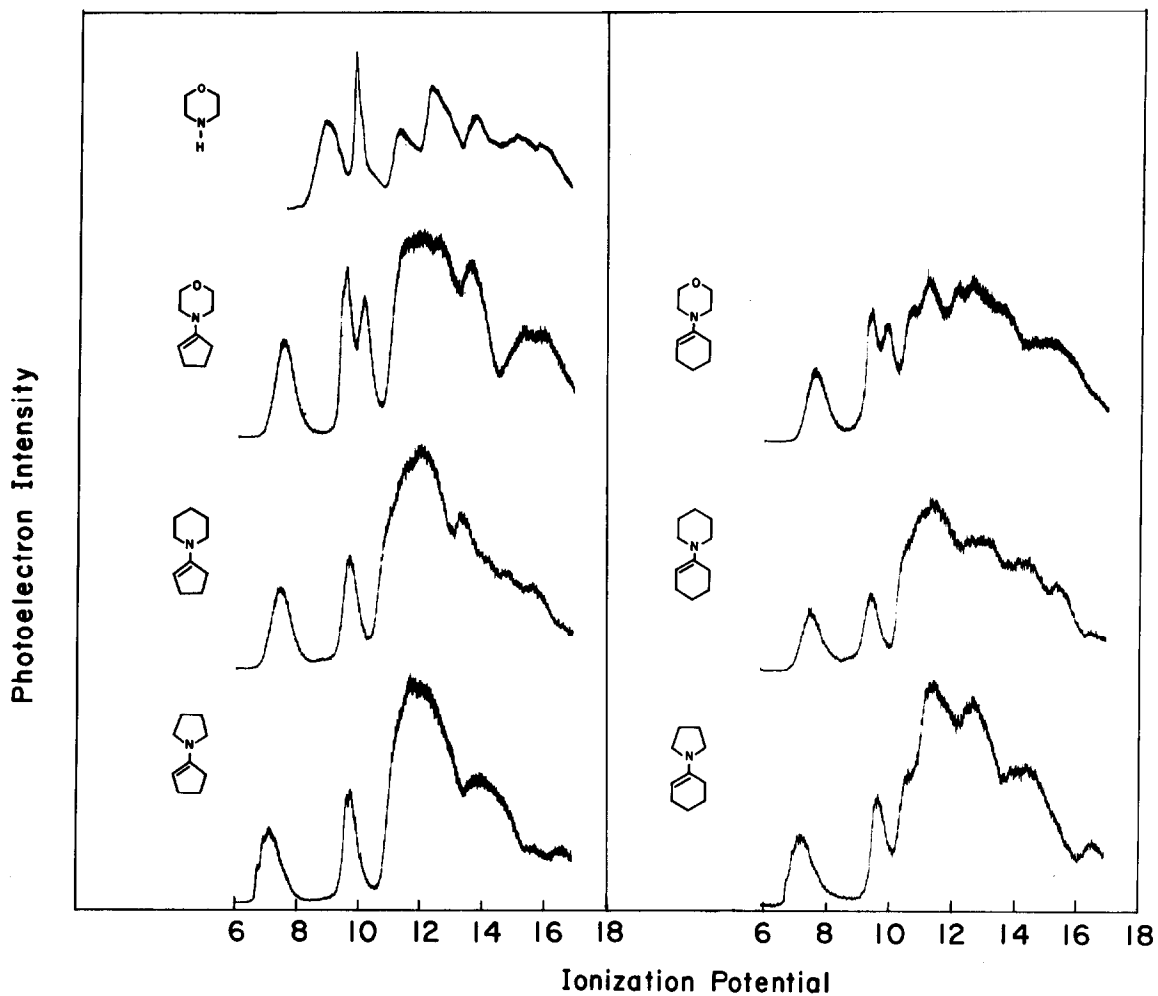
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In the course of a study of the relationships between the electronic structures of enamines and the rates of reactions of these species, we have encountered some differences between IP's reported in the literature and those found in our laboratories. In order to show in a preliminary way how alkene ring-size and the nature of the amine affect enamine IP's, and to give photoelectron spectral evidence for the pyramidal nature of the enamine nitrogen, we report here the photoelectron spectra of the pyrrolidine, piperidine, and morpholine enamines of cyclopentanone and cyclohexanone.

The photoelectron spectra of these six enamines, and of morpholine are shown in the Figure.² Each of the enamines has a broad low energy ionization at 7.1-7.7eV, and a second sharper band at 9.3-9.7eV. The broadness of the first band indicates that it has largely amine lone-pair character, such as that in the first band of morpholine. The broadness of amine lone-pair ionization bands is due to the large difference in geometries between ground-state amines (pyramidal) and their radical cations (planar).^{3,4} Thus, these spectra indicate that the amine portion of enamines is pyramidal. A microwave spectrum of vinylamine was interpreted in this way, also.⁵

The second band in the enamine spectra is somewhat broader than that of the corresponding cycloalkene, but still contains vibrational spacing of 0.16-0.17eV, corresponding to the CC double bond stretching frequency in the radical cation.⁴ This vibrational structure attests to the essentially alkene-like nature of the second ionization band in enamines.

The morpholine enamines have a third band due to the oxygen lone-pair orbital (n_O). In



Photoelectron spectra of (left, top to bottom) morpholine, morpholinocyclopentene, piperidinocyclopentene, pyrrolidinocyclopentene, and (right, top to bottom) morpholinocyclohexene, piperidinocyclohexene, and pyrrolidinocyclohexene.

tetrahydropyran, the n_0 ionization appears at 9.50eV.⁶ In morpholine, it has been shifted to 9.75eV by the inductive effect of the nitrogen and by through-bond coupling with the nitrogen lone-pair. The latter is expected to be smaller than that which splits the oxygen lone pairs in *p*-dioxane by 1.22eV.⁶ In the morpholine enamines, the n_0 band shifts to higher IP's undoubtedly due to the small positive charge induced on nitrogen, which increases its withdrawing ability.

The vertical IP's for enamines measured in this and other work⁷⁻⁹ are listed below. Although the data reported by Itoh *et al.*⁹ are in reasonable agreement with ours, those of Sustmann and

Table: Vertical Ionization Potentials (eV) of Enamines.

Amine	Alkene		
	cyclopentene	cyclohexene	isobutene
Me ₂ N-	7.46, 9.76 ⁷	7.56, 9.70 ⁷	
(CH ₂) ₄ N-	7.10, 9.66 7.3 ⁸	7.14, 9.58(7.4) ⁸ 7.10, 9.51 ⁹ 7.4 ⁸	7.79, 8.97 ⁹
(CH ₂) ₅ N-	7.4, 9.55	7.50, 9.31 7.42, 9.31 ⁹	7.95, 9.25 ⁹
O(CH ₂ CH ₂) ₂ N-	7.60, 10.08 8.9 ⁸	7.67, 9.40, 9.88 7.66, 9.42, 9.91 ⁹	8.20, 9.41, 9.69 ⁹

Trill⁸ deviate considerably from our values. The morpholinocyclopentene value of 8.9eV reported on a graph by Sustmann and Trill is very close to our IP for morpholine (8.88eV). In our experience, small amounts of amine and ketone, formed by inadvertent enamine hydrolysis, had to be pumped from the samples before the spectra of pure enamines could be obtained.

Upon conversion of a dialkylamine to the corresponding enamine, the nitrogen lone-pair will be destabilized by an inductive effect, the result of substitution of an alkenyl group for a hydrogen, and also by the conjugative interaction of the amine lone-pair with a lower energy alkene π orbital. MINDO/2 calculations, performed with and without this conjugative interaction included, indicate that about one-third of the lone-pair destabilization results from the inductive effect. The net experimental destabilization is larger in the cyclopentenes (1.22-1.67eV) and cyclohexenes (1.41-1.63eV) than in the isobutenes (0.68-0.98eV).

The alkene π orbital in the enamine is stabilized slightly by the nitrogen inductive effect and to a larger extent by conjugative interaction with the higher energy amine lone-pair orbital. The change in the IP of the π orbital is smaller than that of the lone-pair, since the alkylamine group has several lower energy orbitals of correct symmetry to interact with the alkene π orbital.

The net increase in π IP is 0.31-0.48eV for the cyclopentenes, 0.18-0.46eV for the cyclohexenes, and 0-0.43eV for the isobutenes. Both these and the lone-pair energy changes indicate a decrease in interaction in this order.

Finally, it is notable that the decrease in enamine first IP follows the increase in reactivity of enamines in electrophilic reactions such as phenylazide cycloaddition,¹⁰ benzyl bromide, methyl acrylate, and acrylonitrile alkylation,¹¹ and cupric chloride oxygenation,⁹ as long as the alkene moiety in the enamine is constant.

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References and Notes

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