Nitrogen Lone Pairs and the Ionization Potentials of Azines and Azoles

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Summary The photoelectron spectra of azoles are discussed in relation to the spectrum of pyridine: the nitrogen lone pair of pyridine is deduced to have an ionization potential of 9·8 ev.

WHEN a nitrogen atom is present in a cyclic aromatic structure, its $2p$ lone pair of electrons may either contribute to the aromatic π-system, as in the case of pyrrole, or be independent of it, as in the case of pyridine and isoxazole. For the latter types of molecule, conflicting theories have been put forward as to the relative ionization potentials of the π and the nitrogen lone-pair electrons. The shapes of bands in the photoelectron spectra of the compounds in question are of little help in resolving the conflicting theories, since they contain no sharp features attributable to the nitrogen lone-pair electrons, as they are in fact appreciably delocalized.[1] It is fairly well established however[2,3] that the lowest ionization potential of pyridine is that of an electron from the highest filled π-level (π_3). This is based on the near identities of the first ionization potentials of benzene, pyridine, and pyrazine. Such a constancy would be expected for the ionization potential of the highest occupied π-orbital throughout the three molecules on account of the nodal properties of this orbital in each case (Figure). The second and third (vertical) ionization potentials of pyridine are about 9·8 and 10·5 ev respectively. In a recent study of the photoelectron spectra of substituted pyridines and diazines, Baker and Turner[3] were unable to decide for certain whether the 9·8 or the 10·5 ev ionization potential corresponded to the nitrogen lone pair.

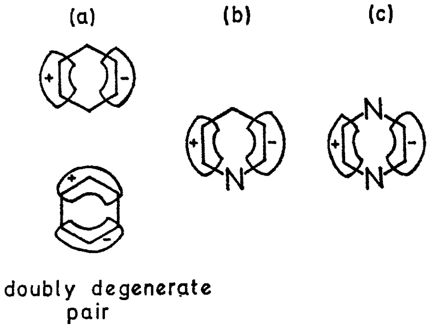

FIGURE. *Forms of the highest occupied π-orbitals in* (*a*) *benzene,* (*b*) *pyridine, and* (*c*) *pyrazine.*

In order to resolve this problem, we have used a photoelectron spectrometer to examine the differences in the π-ionization potentials between the pairs of compounds furan/isoxazole and pyrrole/pyrazole. Since the nitrogen atom in isoxazole, and the nitrogen atom unattached to hydrogen in pyrazole are placed in a region of high electron density with respect to the two highest occupied π-orbitals, the differences between the π-ionization potentials of the two members of each pair of compounds should indicate approximately the magnitude of the difference between the ψ_2 π-orbital ionization potentials of benzene and pyridine, since the ψ_2 π-orbital of the latter compound also has high electron density at the point of nitrogen substitution.

The results for isoxazole, furan, pyrazole, and pyrrole are summarized in the Table. The spectra will be discussed in detail elsewhere,[4] but the point of relevance here is that there has been an appreciable increase in the π-ionization potentials on the introduction of the nitrogen atom to the furan and pyrrole rings. This indicates that the π_2-ionization potential of pyridine is 10·5 ev (benzene π_2-ionization potential = 9·3 ev), and thus the nitrogen lone-pair ionization potential is 9·8 ev. This supports in broad detail the conclusion reached by Heilbronner *et al.*[5] on the basis of the spectrum of 2-trimethylsilylpyridine. It is also consistent with the photoelectron spectrum of MeCH=NEt, which reveals the nitrogen lone-pair ionization potential in this compound is about 9·3 ev[6] (adiabatic value), *i.e.* very similar to that of pyridine.

Lowest ionization potentials of furan, isoxazole, pyrrole, and pyrazole

Compound	Ionization potential (vertical, ev)
Furan	9·0, 10·4
Isoxazole	10·2, 11·3[a]
Pyrrole	8·2, 9·2
Pyrazole	9·5, 10·1, 10·8

[a] The second band in the isoxazole spectrum is approximately twice the intensity of the first band, and thus presumably corresponds to the nitrogen lone pair and the ψ_2 π-electrons.

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