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Roald Hoffmann

Citation: *J. Chem. Phys.* **40**, 2745 (1964); doi: 10.1063/1.1725601

View online: <http://dx.doi.org/10.1063/1.1725601>

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Extended Hückel Theory. II. σ Orbitals in the Azines

ROALD HOFFMANN*

*Chemistry Department, Harvard University
Cambridge, Massachusetts*

(Received 30 January 1964)

FOR many years it has been implicitly assumed that in a molecule such as pyridine the highest occupied molecular orbital is a lone pair on N.¹ On the basis of calculations of the extended Hückel type² for the monocyclic azines it is suggested that the lone-pair concept is inadequate and that the highest occupied σ orbital is considerably delocalized. It should be immediately emphasized that the conclusions are relevant only to the spectroscopic orbital, i.e., the one involved in ionization or $n \rightarrow \pi^*$ transitions. The chemist's loosely defined but extremely useful construct of a lone pair in an organic reaction cannot be analyzed by this method.³

The parameters for carbon and hydrogen are those used previously²: the nitrogen Coulomb integrals were chosen as -13.4 eV ($2p$) and -26.0 eV ($2s$), a rough average of the valence state ionization potentials for the two common N valence states.⁴ Calculations were first carried out on NH_3 , comparing with the SCF results of Kaplan⁵ and Duncan.⁶ For the top filled orbital, a Mulliken population analysis carried out on Duncan's wavefunction yields the gross atomic populations N_{2p} , 1.719; N_s , 0.239; H, 0.014; i.e., a respectable lone pair, mainly p in character. Use of the relation $H_{ij} = K S_{ij} 0.5(H_{ii} + H_{jj})$ with $K = 1.75$ did not give the correct NH_3 geometry,⁷ while use of $H_{ij} = K' S_{ij}$ with $K' = -35$ eV gave a good match of the electron dis-

tribution in the highest occupied orbital and the correct conformation. Calculations were performed with both methods, a variety of azine geometries, and various assumptions about N parameters; the general conclusions are fairly insensitive to these.

Consider a set of sp^2 hybrids in pyridine, oriented as in Fig. 1. Some representative overlap integrals between hybrids⁸ are:

$$\begin{aligned} S_{af} &= 0.0915 & S_{ad} &= 0.1189 & S_{aH} &= 0.0591 \\ S_{ae} &= -0.0996 & S_{cd} &= 0.6704. \end{aligned}$$

Clearly, the presumed lone pair a mixes with other σ orbitals. A typical calculated charge distribution in the highest molecular orbital occupied in pyridine assigns 2.0 electrons as follows: N₁, 1.06; C_{2,6}, 0.18; C_{3,5}, 0.17; C₄, 0.06; H_{3,5}, 0.03; H_{2,6}, 0.03; H₄, 0.06. Over a wide range of parameters, the extent of localization in pyridine, i.e., the fraction of electrons on the nitrogen varies from 25% to 66%. Localization is better in the higher azines. One curious effect is that increase in nitrogen electronegativity, which at first sight would appear to lead to a better localization of electrons about N, in fact brings the top σ orbital to lower energies, where it interacts more strongly with orbitals of the same symmetry, with resultant increased delocalization. Indeed the best lone pair in these calculations was that in C_6H_5^- .

In the delocalized highest σ orbital, the electron density which is on N is mostly in the $2p\sigma$ orbital with less than 10% $2s$ contribution.⁹ In calculations of oscillator strengths for $\sigma \rightarrow \pi^*$ transitions it is found that two center integrals cannot be neglected. The calculated intensities are too small and are sensitive to the parametrization. An extended discussion of the energy levels and electronic distributions may be obtained from the author.¹⁰

I would like to thank J. Goldin for computational assistance. This work was supported by NIH and the Harvard Computation Center.

* Junior Fellow, Society of Fellows, Harvard University.

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⁷ A similar failure of the extended Hückel theory occurs for H_2O , which in the calculation prefers a linear configuration. Raising the H Slater exponent to 1.2 or 1.3 changes the H_2O minimum to an angle $\text{HOH} = 150^\circ$, but has no effect on NH_3 . In Ref. 2 are detailed some objections to the use of the simple relationship $H_{ij} = K' S_{ij}$.

⁸ In a model geometry of a perfect hexagon with side = 1.40 Å, C-H 1.1 Å. The Slater exponents are H, 1.0; N, 1.950; C, 1.625.

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¹⁰ The computer program used in these calculation and those of Ref. 2 is available from the Quantum Chemistry Program Exchange, Chemistry Department, Indiana University.

FIG. 1. Numbering system and schematic indication of direction of sp^2 hybrids in pyridine.

