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π-Electron Approximation in Pyridine and Related Compounds

By

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A semi-empirical LCAO calculation including σ- and π-electrons has been performed for pyridine and related heterocyclics. The diagonal matrix elements of Hamiltonian are evaluated from atomic spectroscopic data through the use of a formula derived from the SCF equations. The non-diagonal matrix elements are estimated through the Wolfsberg-Helmholz formula. All overlap integrals have been included. The results disagree with what one can expect from a π-electron treatment, mainly with respect to population analysis, but they seem strongly supported by the conclusions of "ab initio" calculations for other compounds and the trend of dipole moment in the sequence pyridine, quinoline, acridine.

L'ensemble des systèmes électroniques σ et π de la pyridine et de ses homoogues supérieurs a été étudiée par une méthode LCAO semi-empirique. Les élements de matrice diagonaux de l'hamiltonien sont évalués à partir de données de spectroscopie atomique, en faisant appel à une formule dérivée des équations du champ self-consistant. Les éléments de matrice non diagonaux sont calculés par la formule de Wolfsberg-Helmholz. Toutes les intégrales de recouvrement ont été introduites. Surtout en ce qui concerne l'analyse de population, les résultats sont en désaccord avec ce que l'on peut attendre d'un calcul limité au système d'électrons π; par ailleurs, ils paraissent confirmés par les conclusions de calculs "ab initio" relatifs à d'autres composés et par l'évolution du moment dipolaire dans la série pyridine, quinoléine, acridine.

Für Pyridin und verwandte Heterozyklen wurde eine LCAO-Rechnung mit σ- und π-Elektronen durchgeführt. Die Diagonalelemente des Hamiltonoperators wurden mittels atomspektroskopischer Daten berechnet unter Benutzung einer aus SCF Rechnungen abgeleiteten Formel, die Nicht-Diagonalelemente mit der Wolfsberg-Helmholz-Formel. Alle Überlappungsintegrale wurden berücksichtigt. Die Ergebnisse stimmen mit solchen aus π-Elektronen-Behandlungen nicht überein (besonders die Dichteverteilung), scheinen aber stark durch "ab initio"-Rechnungen für andere Verbindungen und das Verhalten des Dipolmoments in der Folge Pyridin, Chinolin, Acridin gestützt zu werden.

It is a common assumption that, in conjugated heterocyclics like pyridine, the π-electron system can be studied from the quantum point of view without taking into account explicitly the σ-system (see for instance [*18*]). Such an assumption has been used in the oversimplified Hückel procedure as well as in some more sophisticated methods like the Parr-Pariser-Pople. This simplification relies on the fundamental hypothesis that the mutual interaction of the systems σ and π can be neglected. It has been noticed that this hypothesis is probably less valid for conjugated heterocyclics than for the aromatic hydrocarbons themselves (see for instance [*18*]). A quantum study of the whole electronic system of pyridine would be of interest in as much as it allows to have an idea of the validity of the previous hypothesis. A recent paper by Hoffmann deals with the electronic structure of

σ orbitals in pyridine [9], but is mainly centered on the nature of the lone pair. We have performed another study and, due to some differences in the theoretical method, our results are different from those of Hoffmann's paper for at least one important point.

We shall report here only the main features of the theoretical method we used; some detailed accounts have been given elsewhere [3. 4]. The atomic basis orbitals are Slater orbitals $2s$ and $2p$ for the C and N atoms, $1s$ for the H atoms, with usual Slater exponents [25]. We used a monoelectronic effective Hartree-Fock hamiltonian. The corresponding diagonal matrix element for the p orbital of atom P is given by:

$$H_{pp} = W_p + \sum_{r \in P} q_r \left(J_{pr} - \tfrac{1}{2} K_{pr}\right)$$

where:

W_p includes the kinetic term and the core interaction term (the core is made from the nucleus for the H atoms, the nucleus plus the $1s$ electrons for the C and N atoms);

the summation $\sum_{r \in P}$ is carried over every orbital r from the P atom which is not included in the core;

q_r is the orbital population, as defined by Mulliken [17], for the orbital r;

J_{pr} and K_{pr} are the atomic coulomb and exchange integrals.

This formula has been deduced from the Roothaan's SCF equations [23], using in a systematic manner the Mulliken and Ruedenberg approximations [24].

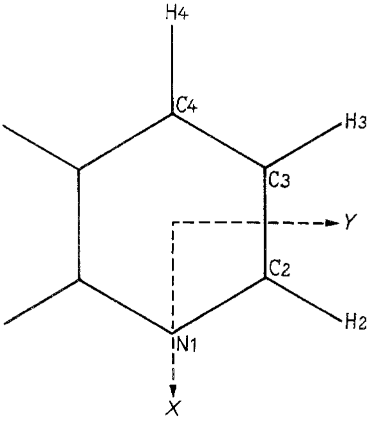

Fig. 1

Using this expression, the matrix elements H_{pp} can be computed in a semi-empirical manner from the atomic valence-state energies, using the values given by Pilcher and Skinner [21]. The details of the procedure have been given elsewhere [3]. The matrix elements H_{pp} depend explicitly on the orbital populations q_r: so we can be confident of the results of the calculation only if the populations which are carried out from the calculation agree with those used for the computation of the H_{pp} elements (at least within a certain accuracy); if this condition is not fulfilled, another trial with a new set of q_r should be made. We asked for an accuracy of 0.01 electron.

The non-diagonal matrix elements have been evaluated through the Wolfsberg-Helmholz formula [*26*]:

$$H_{pq} = \tfrac{1}{2}\, K\, S_{pq}\, (H_{pp} + H_{qq})\,.$$

All the overlap matrix and all the non-diagonal matrix elements have been introduced. We use for the Wolfsberg-Helmholz constant the value $K = 3$, which gave us previously satisfactory results [*3*]. The geometry used is that derived by BAK *et al.* from a microwave study [*2*]. The numbering and the choice of coordinate axes are given in the figure.

Our discussion will be centered on results relative to the electronic density: the orbital populations, the total and formal atomic charges are given in Tab. 1.

Table 1

Atom	Orbital Population				Total Charge	Formal Charge
	1*s* or 2*s*	2 *px*	2 *py*	2 *pz*		
N1	1.29	1.86	1.13	0.91	5.19	−0.19
C2	1.01	0.96	0.94	1.11	4.02	−0.02
C3	1.03	1.03	1.06	0.94	4.06	−0.06
C4	1.02	1.06	0.98	0.98	4.04	−0.04
H2	0.93				0.93	+0.07
H3	0.91				0.91	+0.09
H4	0.92				0.92	+0.08

The most noticeable result pertains to the populations of the $2p\pi$ orbitals; whereas the $2p\pi$ orbital population is less than one for the nitrogen atom, it is greater than one for the C2 atom. Clearly this result contradicts what is generally expected from a study of the π-electron system either through the Hückel procedure or the Parr-Pariser-Pople one (the same remark applies to the π-electron distribution on the C3 and C4 atoms). So, it is of even more interest to compare our results with some more or less similar conclusions which have been attained by other authors. From a population analysis consecutive to an "ab initio" LCAO SCF calculation for HCN* [*15*], MCLEAN concluded that the nitrogen atom, while bearing a negative formal charge due to the σ-electrons, loses some π charge which is gained by the carbon atom. In a more general study, CLEMENTI and CLEMENTI attained some similar conclusions for C_2N_2 and CO [*7*]. In a general manner, they distinguished between two charge transfer processes: "the one-way and the two-way process" or the "reinforcement charge transfer and opposition charge transfer". As they stated, "in the reinforcement process, observed between same atoms, the σ and π charge transfer cooperate and reinforce each other; they have opposite effects in the opposition process, observed between different atoms". We might say that the group N1–C2 in pyridine (in as much as we can isolate it from the whole system) exhibits an opposition charge transfer. Another general discussion of such results has been given [*19*] by PETERS, who has pointed out the same situation in formaldehyde, using the results of an "ab initio" calculation by

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*	N	C
$2s$	1.77	1.06
$2p\sigma$	1.37	1.04
$2p\pi$ ($2p\bar{\pi}$)	0.97	1.03

FOSTER and BOYS [*8*]: in formaldehyde also, π charge accumulates on carbon rather than on oxygen. It is pleasant that some more or less similar conclusions relative to the electron transfer have been attained either through "ab initio" calculations, either through the method used here which is fundamentally a semi-empirical one and which appeals finally to atomic spectroscopic data.

It should be emphasized that our results are directly linked to the formula which we used for the evaluation of the diagonal elements H_{pp} of the hamiltonian; this formula takes explicitly into account the Coulomb repulsions of the different atomic populations. Instead, this is not the case for instance in the procedure used by HOFFMANN [*9*]: these elements are put equal to either one or an average of valence state ionization potentials for the neutral atom and do not depend on the populations of the different orbitals. KATO *et al.* concluded that, at least for NO_2, the Hoffmann procedure fails in giving the right charges [*11*].

In a further examination of Tab. 1, we can notice that the total charge $\sigma + \pi$ brings some strong resemblance with what is commonly expected from a Hückel calculation for pyridine: the order of decreasing total charge is N, C3, C4, C2. PETERS stated [*19, 20*] that the mathematical apparatus of the Hückel π-electron theory is in some way representing the behaviour of all the electrons in the system. This idea seems strongly supported by our results. Incidentally, PETERS also discussed [*20*] the relationship between the unexpected results of MCLEAN and CLEMENTI for HCN and C_2N_2, and the fact, deduced from nuclear quadrupole resonance data, that the σ charge per hybrid AO at the N atom in pyridine is greater than the π charge [*13*].

A discussion of the dipole moment is specially pertinent in order to have an idea of the validity of the charge distribution. Using the ponctual charge approximation, the theoretical dipole moment of pyridine is found equal to 1.94 D, while the experimental value is 2.2 D (for benzene solution) [*14*]. Three recent papers deal with the dipole moment of pyridine. In the paper by BERTHOD and PULLMAN [*5*], π and σ systems are treated independently through the Hückel method and the DEL RE method: although their charge distributions are fundamentally different from those given in this paper, their σ and π components for the dipole moment are rather similar to ours (Tab. 2). This is no longer true of the values given either by KIER [*12*], who in principle uses the same method as BERTHOD and PULLMAN, or by PUJOL and JULG, whose treatment [*22*] takes into account only the π-electron system and the lone pair of nitrogen.

Of more interest is a study of the dipole moment in the sequence pyridine, quinoline, acridine. Theoretical studies using the π-electron approximation and assuming a fixed σ moment have failed to explain the observed decrease of the dipole moment from pyridine to acridine [*10, 1*]. Results of Tab. 2 show that our

Table 2

	$\mu_{\sigma x}$	$\mu_{\pi x}$	μ_x	$\mu_{\sigma y}$	$\mu_{\pi y}$	μ_y	μ_{th}	μ_{exp}[a]
Pyridine	1.29	0.65	1.94				1.94	2.2
Quinoline	1.31	0.42	1.73	0.58	0.	0.58	1.83	2.2
Acridine	1.29	0.20	1.49				1.49	1.9

[a] Values for solution in benzene, Ref. [*14*].

method accounts for this decrease, which is even slightly overestimated. Once more, this result is related to the mutual interaction of the σ and π systems which our method takes explicitly into account: for instance, method of ref. [*5*], which treats independantly the σ and π systems, fails also to reproduce the experimental decrease [*6*].

As a conclusion, we can state that our calculation does not support the validity of a π-electron treatment for pyridine: the population analysis disagree with what one can expect from a study limited to the π-electron system and seems supported by "ab initio" calculations for smaller compounds and by the trend of the dipole moment on going from pyridine to acridine. We can only emphasize the need of a non-empirical, "ab initio" calculation not only for benzene [*16*], but also for pyridine.

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