APPLICATION OF THE METHOD OF MOLECULAR ORBITALS TO INVESTIGATING THE EFFECTS OF CONJUGATION BETWEEN PHENYL AND 5-MEMBERED N-HETEROATOM RINGS

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Using a Hückel approach in conjunction with the LCAO MO method, calculations are made of \( \pi \)-electron configurations for a number of N- and C-phenyl derivatives of 5-membered nitrogen heterocyclic rings. Using these results, interaction effects between phenyl and heterocyclic ring systems are considered, as well as UV spectra, dipole moments, and reactivities of the compounds investigated.

Studies of reactivities and physical characteristics of N-arylated azoles reveal a quite sharply defined interaction effect between conjugated \( \pi \)-electron systems of the benzene and heterocyclic rings. Thus, for example, the increased ease of opening of the imidazole ring of N-arylimidazoles by nucleophilic reagents is described [1, 2], and N-substitution proceeds for C-arylimidazoles [3, 4] with unexpected difficulty. One of us previously explained these results by analyzing the values of the dipole moments [5] and electronic absorption spectra [6] of N-arylimidazoles. In the present paper, attempts are made to give a more detailed interpretation of the various manifestations of interaction between aryl and azole rings within the framework of the method of molecular orbitals.

Parameters

In computing electron structures of molecules of nitrogen heteroaromatic compounds by the LCAO MO method, the basic problem is choice of suitable Coulomb integrals, \( \alpha \), for the pyrrole and pyridine nitrogen atoms. The values of the Coulomb integrals used by a number of authors for the N atom of pyridine vary from \( \alpha_N + 2.080 \) to \( \alpha_N + 0.280 \), and, in the case of the pyrrole N atom, from \( \alpha_N + 2.780 \) to \( \alpha_N + 0.280 \). Orgel's parameters [7-9] are most widely accepted, though they also give excessively high values of \( \pi \)-electron charges on atoms. Parameters recently put forward [10], \( \alpha_{NH} = \alpha_N + 2.7080 \) and \( \alpha_{-N} = \alpha_0 + 0.3880 \), are attractive, but up to the present they have been checked for only a small range of compounds. The present paper uses "optimal" values of Coulomb and resonance integrals recommended by Streitwieser [11], and equal to

\[
\begin{align*}
\alpha(C) &= \alpha_0, \\
\alpha(-N-) &= \alpha_0 + 0.5\beta_0, \\
\alpha(-N-) &= \alpha_0 + 1.5\beta_0, \\
\beta(C-C) &= \beta_0, \\
\beta(C-N) &= 0.8\beta_0.
\end{align*}
\]

A correction for the inductive effect which the hetero atom has on an adjacent carbon atom, is neglected. The secular determinant was resolved on an ETVM M-20 instrument.

Results

Figures 1a and b, and Fig. 2 show the calculated \( \pi \)-electron charges and mobile bond orders in the ground and first excited states of molecules of pyrrole, imidazole, pyrazole, 1, 2, 4-triazole, benzimidazole, indazole, and their phenyl derivatives. Table 1 gives the energy \( E \) of occupied molecular orbitals, \( \pi \)-electron energies, \( E^\pi \), and the interaction energy \( E^\pi_{in} \) for phenyl and heterocyclic rings. The latter were obtained by subtracting the total \( \pi \)-electron energies of isolated benzene and heterocycles from the total \( \pi \)-electron energy of the corresponding phenyl derivative.

Table 2 compares \( E^\pi_{-in} \), the calculated energy of \( \pi-\pi^* \)-electron transition of some compounds from the ground state to the first excited state, with that found from the long-wave UV absorption bands of the corresponding compounds.

Starting from the distribution of \( \pi \) electrons in the molecules, it proved possible to evaluate the additional \( \pi \) moment arising through interaction of the phenyl and heterocyclic rings; \( \mu_{\pi} = \mu_{\pi}^{\text{phenylazol}} + \mu_{\pi}^{\text{azole}} \). To simplify calculations, we regarded the 5-membered ring as a regular pentagon. All bonds were assumed to be equal in length, 1.39 Å. The values of the \( \sigma \) moments of the bonds for the calculated total dipole moments of the compounds (Table 3) were taken from [7].
Fig. 1a. \( \pi \)-Electron charges and mobile bond orders for the molecules of heterocyclic compounds and their phenyl derivatives.

**Discussion of Results**

**a) Interaction energy of conjugated systems**

Characteristic of N-phenyl derivatives of pyrrole, imidazole, pyrazole, 1, 2, 4-triazole, benzimidazole, and indazole is approximately equal interaction energy for the two aromatic systems, amounting to an average of 0.22 kcal/mole. Taking the value of the standard resonance integral \( B^0 \) as 20 kcal/mole [11], the interaction energy comes out at 4.3–4.5 kcal/mole, in approximate agreement with the value of 4 kcal/mole, which we deduced from UV spectrum data for N-phenylbenzimidazole [6]. This value is half the interaction energy of the \( \pi \) systems of the two phenyl groups in diphenyl [12], but it is not unexpected, since formally, in the ground state of the molecules of N-phenyl derivatives of 5-membered nitrogen heterocycles (FNH), the double bonds of the benzene and heterocyclic rings are not conjugated. In terms of the valence bond method, this means that the contribution of the ionic structures of type II, where such conjugation occurs, to the ground state of the molecules of the N-phenyl derivatives of FNH is relatively small. The low orders of the mobile N-C\textsubscript{phen} bonds for all compounds (Figs. 1a, b) support this view.

Considerably more effective (almost twice as much so) is \( \pi \) interaction of aromatic rings in C-phenyl derivatives of FNH, where the double bonds of the benzene and heterocyclic rings are conjugated in the ground state. The interaction energy of rings of the C-phenyl derivatives can be calculated as 7.5–8.5 kcal/mole, in agreement with the interaction energy of the two phenyl rings in diphenyl.

The somewhat lower \( \pi \) interaction energy in 2-phenylpyrrole is evidently due to the lower aromaticity of the pyrrole ring, as it is known that the conjugation of 2 ring systems is greater, the lesser their internal conjugation [9].

The \( \pi \) interaction energy of the rings is somewhat greater for 4-phenylimidazole than for 2-phenylimidazole, despite the latter’s having an unbranched system of conjugated bonds (head-to-tail type of ring connection), while 4-phenylimidazole has a cross-conjugated system. Apparently the effect observed indicates that in 2-phenylimidazole conjugation of the phenyl group with the \( \pi \)-electron system of the imidazole ring is to a considerable extent effected not only through the pyridine nitrogen atom, but also through the pyrrole one. This view finds support from the lower basicity of 4-phenylimidazole (\( pK_a \) 6.10) as compared with 2-phenylimidazole (\( pK_a \) 6.48) [13].

**b) Electronic absorption spectra**

Unlike unsaturated heterocyclic systems, N-phenyl derivatives of pyrrole, pyrazole and 1,2,4-triazole are