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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 π-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 π-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, α, 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 $\alpha^0 + 2.0\beta^0$ to $\alpha^0 + 0.2\beta^0$, and, in the case of the pyrrole N atom, from $\alpha^0 + 2.7\beta^0$ to $\alpha^0 + \beta^0$. Orgel's parameters [7–9] are most widely accepted, through they also give excessively high values of π-electron charges on atoms. Parameters recently put forward [10], ($\alpha_{NH} = \alpha^0 + 2.70\beta^0$ and $\alpha_{-N=} = \alpha^0 + 0.38\beta^0$), 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

$$\begin{aligned} &\alpha(\mathrm{C}) = \alpha^0; && \beta(\mathrm{C-C}) = \beta^0; \\ &\alpha(-\mathrm{N}=) = \alpha^0 + 0.5\,\beta^0; && \beta(\mathrm{C-N}) = 0.8\,\beta^0. \\ &\alpha(-\mathrm{N}\langle\,) = \alpha^0 + 1.5\,\beta^0; && \end{aligned}$$

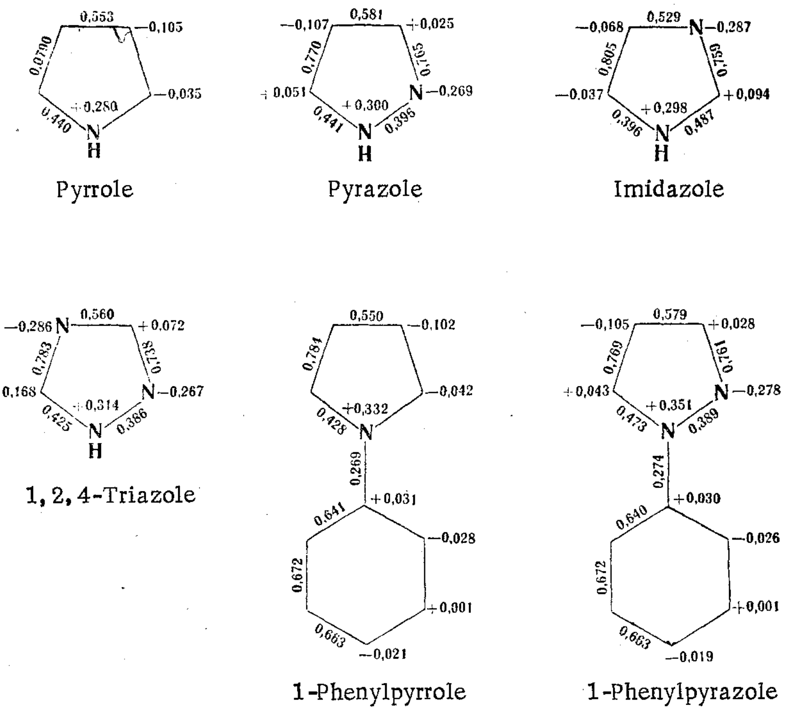
A correction for the inductive effect which the hetero atom has on an adjacent carbon atom, is neglected. The secular determinant was resolved on an ETsVM M-20 instrument.

Results

Figures 1a and b, and Fig. 2 show the calculated π-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, π-electron energies, E^{π}, and the interaction energy E^{π}_{in} for phenyl and heterocyclic rings. The latter were obtained by subtracting the total π-electron energies of isolated benzene and heterocycles from the total π-electron energy of the corresponding phenyl derivative.

Table 2 compares $E^{\pi-\pi^*}$, the calculated energy of π-π^*-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 π electrons in the molecules, it proved possible to evaluate the additional π moment arising through interaction of the phenyl and heterocyclic rings: $\vec{\mu}^{\pi}_{in} = \vec{\mu}^{\pi}_{N}$-phenylazole$-\vec{\mu}^{\pi}$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 σ moments of the bonds for the calculated total dipole moments of the compounds (Table 3) were taken from [7].



Pyrrole Pyrazole Imidazole

1, 2, 4-Triazole 1-Phenylpyrrole 1-Phenylpyrazole

Fig. 1a. π-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 $0.22\beta^0$. Taking the value of the standard resonance integral β^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 π 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 $N-C_{phen}$ bonds for all compounds (Figs. 1a, b) support this view.

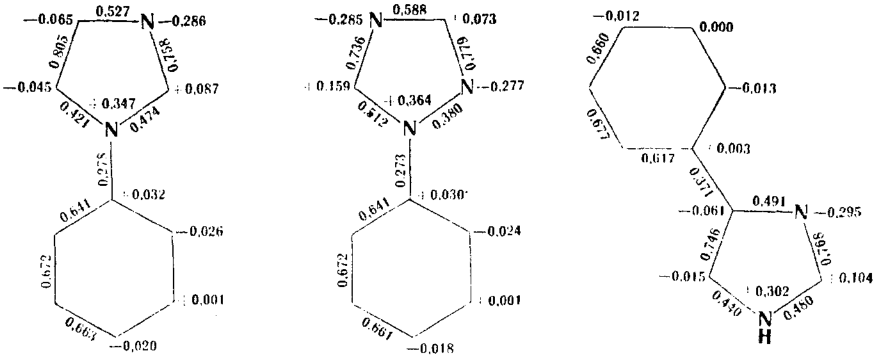
Considerably more effective (almost twice as much so) is π interaction of aromatic rings in C-phenyl derivatives of FNH, where the double bonds of the benzene and heterocyclic rings are conjugated in the ground state. The interaction energy of rings of the C-phenyl derivatives can be calculated as 7.5–8.5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

The somewhat lower π 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].

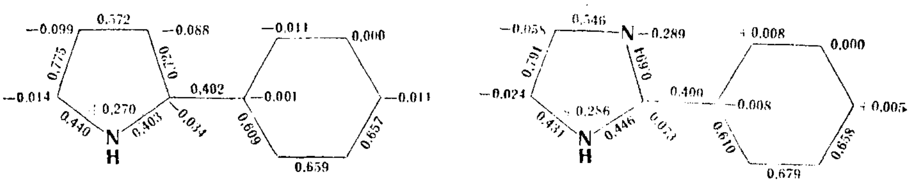
The π interaction energy of the rings is somewhat greater for 4-phenylimidazole than for 2-phenylimidazole, despite the latter's having an unbranched system of conjugated bonds (head-to-tail type of ring connection), while 4-phenylimidazole has a cross-conjugated system. Apparently the effect observed indicates that in 2-phenylimidazole conjugation of the phenyl group with the π-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

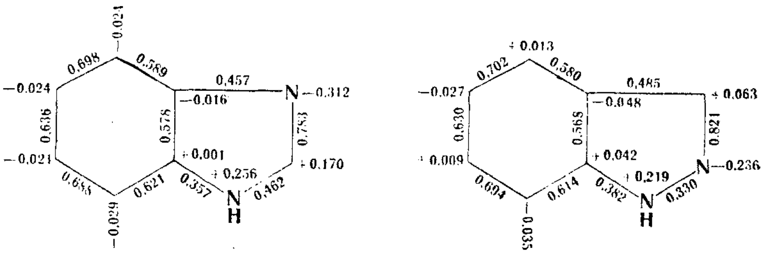
Unlike unsaturated heterocyclic systems, N-phenyl derivatives of pyrrole, pyrazole and 1, 2, 4-triazole are



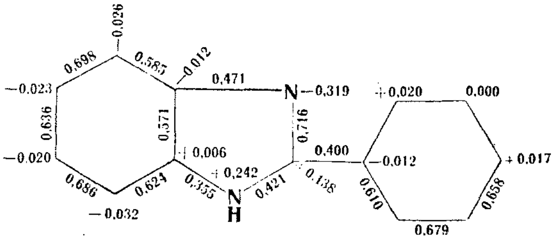
1-Phenylimidazole 1-Phenyl-1, 2, 4-triazole 4-Phenylimidazole



2-Phenylpyrrole 2-Phenylimidazole



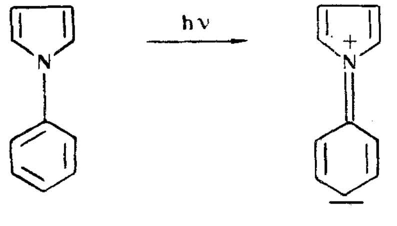
Benzimidazole Indazole



2-Phenylbenzimidazole

Fig. 1b. π-Electron charges and mobile bond orders of heterocyclic molecules and their phenyl derivatives.

characterized by an intense absorption band in the 235–255 mμ* region, regarded by various authors as a K-band [6, 14–16]. Our calculations of the electron structure of the first excited state of the molecules of these compounds (Fig. 2) also show that excitation is connected with passage of electron density from one aromatic ring to the other, and the nature of the charge transfer in no case corresponds to the aniline-like shift I → II, as postulated by the authors of the papers mentioned above:



I II

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*1-Phenylimidazole also has an indistinct absorption band in the form of a shoulder in the 265 mμ region (lg ε 3.27)[6].

Table 1

Energies of Bonding Molecular Orbitals, π-Electron Energies, and Interaction Energies of Aromatic Rings of Azoles and Phenylazoles

Compound	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8	$E^{\pi *}$	$E^{\pi **}_{in}$
Pyrrole	−2.3196	−1.1887	−0.6180	—	—	—	—	—	8.2528	—
Pyrazole	−2.4065	−1.1978	−0.8105	—	—	—	—	—	8.8296	—
Imidazole	−2.3737	−1.3785	−0.6736	—	—	—	—	—	8.8516	—
1, 2, 4-Triazole	−2.4540	−1.3789	−0.8814	—	—	—	—	—	9.4286	—
Benzimidazole	−2.5311	−1.7736	−1.4726	−0.8565	−0.7086	—	—	—	14.6848	—
Indazole	−2.4984	−1.7793	−1.3711	−0.8923	−0.7363	—	—	—	14.5546	—
1-Phenylpyrrole	−2.5691	−1.9250	−1.3336	−1.0000	−0.7891	−0.6180	—	—	16.4696	0.2168
1-Phenylpyrazole	−2.6244	−1.9473	−1.3540	−1.0000	−0.8194	−0.7803	—	—	17.0508	0.2212
1-Phenylimidazole	−2.5932	−1.9574	−1.4875	−1.0000	−0.8283	−0.6674	—	—	17.0676	0.2166
1-Phenyltriazole	−2.6485	−1.9750	−1.4890	−1.0000	−0.9319	−0.7803	—		17.6494	0.2208
1-Phenylbenzimidazole	−2.6790	−2.0777	−1.7578	−1.5003	−1.0000	−1.0000	−0.7709	−0.6666	22.9046	0.2198
1-Phenylpyrazole	−2.6560	−2.0573	−1.7632	−1.4149	−1.0000	−1.0000	−0.8641	−0.6354	22.7816	0.2270
2-Phenylpyrrole	−2.4580	−1.9973	−1.2596	−1.1511	−1.0000	−0.4706	—	—	16.6728	0.4202
2-Phenylimidazole	−2.5071	−2.0013	−1.3845	−1.1861	−1.0000	−0.5354	—	—	17.2288	0.3770
2-Phenylbenzimidazole	−2.6107	−2.0773	−1.7677	−1.4996	−1.1657	−1.0000	−0.8302	−0.5995	23.1014	0.4166
4-Phenylimidazole	−2.4734	−2.0572	−1.1502	−1.0458	−1.0000	−0.5392	—	—	17.2362	0.3846

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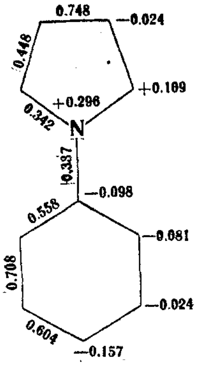
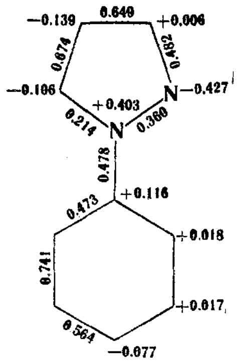
* E_1–E_8 values given in $\frac{\alpha^0 - E}{\beta^0}$ units

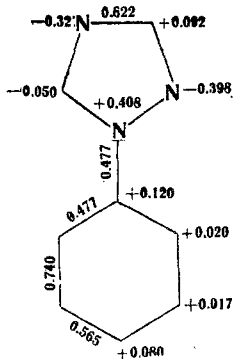
** E^{π} and E^{π}_{in} given in $\beta°$ units.



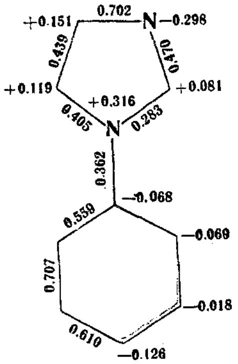
1-Phenylpyrrole



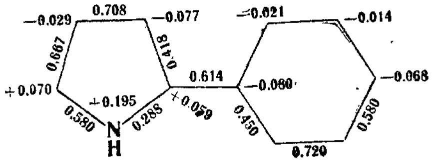
1-Phenylpyrazole



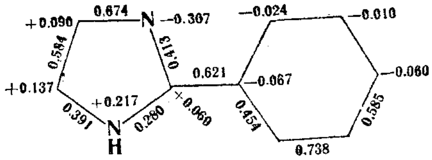
1-Phenyl-1, 2, 4-triazole



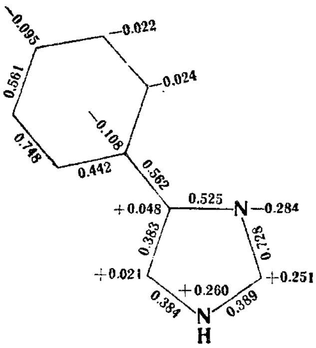
1-Phenylimidazole



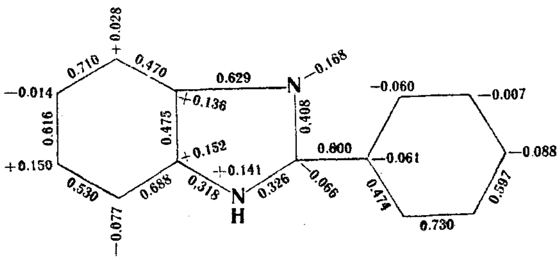
2-Phenylpyrrole



2-Phenylimidazole



4-Phenylimidazole



2-Phenylbenzimidazole

Fig. 2. Electron charges and mobile bond orders for molecules of phenyl derivatives of 5-membered nitrogen heterocycles in the first excited state.

Thus, for example, the excitation of N-phenylpyrrole is connected with shift of electron density from the diene system of the pyrrole ring to the :$N-C_6H_5$ group, while, in the cases of N-phenylpyrazole and 1-phenyltriazole, excitation involves reverse shift of electron density from the :$N-C_6H_5$ group to the diene system. More complex transition is observed in 1-phenylimidazole: on excitation, one part of the diene system ($C_4{=\!=}C_5$) behaves as a donor, and another ($C_2{=\!=}N_3$) as an acceptor of electrons. The total effect, as for 1-phenylpyrrole, here comprises supplying electrons to the benzene ring. Thus, with increasing number of N-heteroatoms in the heterocyclic system (pyrrole– pyrazole, imidazole–triazole), its electron donor properties are weakened, which seems quite natural in view of the higher electronegativity of nitrogen in comparison with carbon. Often this shows up in the ground state of molecules of N-phenylated heterocycles, and particularly clearly when they are excited (Table 2).

Table 2

Energies of $\pi \rightarrow \pi^*$ Electron Transitions and the Position of the Longwave Absorption Band of Phenyl Derivatives of 5-membered Nitrogen Heterocycles

Compound	$E^{\pi \rightarrow \pi^*}$ *	Total charge on the phenyl group in the ground and excited states		λ_{max}, mμ (lg ε)	Reference
1-Phenylpyrrole	−1.4832	−0.046	−0.465	253 (4.13)	16
1-Phenylpyrazole	−1.5337	−0.039	+0.109	257 (4.08)	15
1-Phenylimidazole	−1.4982	−0.038	−0.368	243 (3.84)	6
1-Phenyltriazole	−1.5148	−0.034	+0.274	239 (4.04)	14
2-Phenylpyrrole	−1.1802	−0.034	−0.218	287 (4.08)	17
2-Phenylimidazole	−1.1782	+0.013	−0.195	271 (4.2)	18
4-Phenylimidazole	−1.3504	−0.035	−0.295	257 (4.2)	19

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* $E^{\pi - \pi^*}$ given in β^0 units.

Table 3

Dipole Moments of N-Phenylazoles (in Debyes)

Compound	μ^π, Θ*	μ^σ, Θ	μ, Θ	$\mu_{in}^{\pi,\Theta}$	μ_{exp} **
1-Phenylpyrrole	1.69; 0°	0.08; 0°	1.61; 0°	0.74; 0°	1.32 1.61
1-Phenylimidazole	2.77; 5°	0.87; 39°	3.52; 13°	0.68; 0°	3.14
1-Phenylpyrazole	1.65; 51°	0.95; 115°	2.27; 73°	0.59; 0°	—***
1-Phenyltriazole	2.34; 29°	0.50; 41°	2.84; 32°	0.56; 0°	2.89

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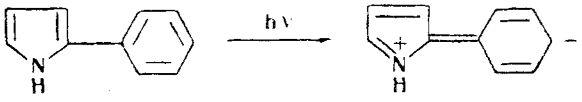
* Slope angle which the dipole moment vector makes with an axis passing through the N_1 atom of the 5-membered ring and the para carbon atom of the phenyl group.

** Experimental values of dipole moments taken from a manual [22] and a paper [5].

*** Just after the present paper had been received by the editor, a paper [25] dealt with measuring the dipole moment of 1-phenylpyrazole. The value obtained (2.001) also agrees satisfactorily with the value predicted by us.

Since the character of the electron shifts when molecules of N-phenyl derivatives of FNH are excited varies, one would not expect any correlation between interaction energies of aromatic systems or energies of $\pi \rightarrow \pi^*$ transitions, on the one hand, and the position of the longwave absorption band of these compounds, on the other.

In agreement with the high value of the interaction energy of aromatic rings in the ground state of molecules of 2-phenyl FNH derivatives, their longwave absorption band is appreciably displaced towards the red as compared with the analogous bond of the N-phenyl substituted compounds. As consideration of the electron structure of the first excited state of molecules of 2-phenyl derivatives of pyrrole and imidazole shows, the longwave absorption band of these compounds can be related to shift of π electron density from the heterocyclic ring to the phenyl group, e.g., III → IV:



III IV

For 2-phenylbenzimidazole, the longwave absorption band lies in the region of yet longer wavelength [18] as compared with 2-phenylimidazole, and this is due to the longer conjugation chain and the high E^{π}_{in} values for the phenyl and imidazole rings. Here, π-electron transition is mainly connected with charge transfer from the benzene ring annelated with the heterocyclic ring, to the 2-phenyl substituent. This confirms the validity of considering similar 2-arylbenzazoles as planar models of aromatic Schiff's bases when analyzing the spectra of the latter [20].

Considering the relative values of E^{π}_{in}, it is difficult to explain why the longwave absorption band of 4-phenylimidazole occurs in the lower wavelength region as compared with the same band of 2-phenylimidazole.

c) Dipole moments

Calculated values of dipole moments of N-phenylazoles (Table 3) $\vec{\mu} = \vec{\mu}^{\pi} + \vec{\mu}^{\sigma}$, are in completely satisfactory agreement with experimental values, which can be considered as additional support for the parameters for the hetero atoms which we chose. In agreement with previously stated considerations [5], calculations show that conjugation of the N-phenyl and heterocyclic rings gives rise to an additional π moment, directed along the N-Ph axis, and calculated from the total moment of the heterocyclic part of the molecule. This leads to the conclusion that the dipole moments of N-phenyl FNH derivatives are lower than the dipole moments of unsubstituted or N-methylated heterocyclic rings. The value of the additional π moment μ^{π}_{in} calculated by us, is a maximum for 1-phenylpyrrole and a minimum for 1-phenyltriazole, i.e., increases with the number of hetero atoms in the molecule. The values of μ^{π}_{in} calculated for 1-phenylpyrrole and 1-phenylimidazole are in good agreement with those previously arrived at from experimental data [5, 21].

d) Reactivity

The electron density distribution for the ground state of molecules of N-phenyl FNH derivatives indicates that the heterocyclic ring must be ortho-, para-directing for electrophilic substitution in the benzene part of the molecule. Experimental results for nitration of 1-phenyl derivatives of imidazole, pyrazole, and indazole, are in accord with that view [23]. Judging by the total π-electron charges localized in the benzene ring, the ortho-, para-orientating capacity of heterocyclic rings decreases in the order pyrrole, imidazole, pyrazole, 1, 2, 4-triazole.

Ortho-, para-activation in the phenyl group is also found in 2-phenylpyrrole and 4-phenylimidazole. However, for 2-phenylimidazole, and particularly for 2-phenylbenzimidazole in the ground state, deactivation of the benzene ring is observed, so that here mainly meta orientation is to be expected. Results [24] show that nitration of 2-phenylimidazole gives a mixture of o-, m-, and p-nitrophenyl derivatives in the ratios 7.5 : 1 : 250. This kind of disagreement between experimental and calculated results for very small changes in the π electron charges, has been found by other authors [9]. There are no experimental results for electrophilic substitution in the 2-phenyl group of 2-phenylbenzimidazole.

Molecular orbital calculations show that N-phenyl and C-phenyl groups should not have a substantial effect on the reactivities of heterocyclic rings. This confirms the previously expressed view regarding the steric nature of the hindrance, shown by phenyl in the N-substitution of 2-phenylbenzimidazole and 4-phenylimidazole [4].

On the other hand, in contrast to the conclusions previously drawn from experimental results obtained with N-phenylimidazoles [1, 2], the phenyl group, as the calculations show, not only does not lower, but even increases several-fold the π-electron density at Cμ as compared with that in the non-phenylated compound. Obviously, the character of the reaction taking place at Cμ in the imidazole ring is to a large extent determined by the distribution of electron density in the reaction transition state.

REFERENCES

1. A. M. Simonov, N. D. Vitkevich, and S. Ya. Zheltonozhko, ZhOKh, 30, 2688, 1960.
2. A. M. Simonov and A. F. Pozharskii, ZhOKh, 33, 2350, 1963.
3. L. N. Pushkina, S. A. Mazalov, and I. Ya. Postovskii, ZhOKh, 32, 2625, 1962.
4. A. F. Pozharskii, Master's Thesis, Rostov-on-Don State University, 1963.

5. A. F. Pozharskii and A. M. Simonov, ZhOKh, 34, 224, 1964.
6. A. F. Pozharskii, ZhOKh, 34, 630, 1964.
7. L. E. Orgel, F. L. Cottrell, W. Dick, and L. E. Sutton, Trans. Farad. Soc., 47, 113, 1951.
8. A. J. Owen, Tetrahedron., 14, 237, 1961.
9. G. Del Re, J. Chem. Soc., 3324, 1962.
10. H. Hamano and H. Hameka, Tetrahedron., 18, 985, 1962.
11. A. Streitwieser, Molecular Orbital Theory, N.Y., 1961.
12. L. Pauling and Sherman, J. Chem. Phys., 1, 606, 679, 1933.
13. H. Walba and R. W. Isensee, J. Org. Chem., 26, 2789, 1961.
14. M. R. Atkinson, E. A. Parkes, and J. B. Polya, J. Chem. Soc., 4256, 1954.
15. D. D. Monte, A. Mangini, and A. Passerini, Gazz. chim. ital., 86, 797, 1956.
16. D. D. Monte, A. Mangini, R. Passerini, and C. Zauli, Gazz. chim. ital.,, 88, 977, 1958.
17. B. Elpern and F. C. Nachod, J. Am. Chem. Soc., 72, 3379, 1950.
18. G. Leandri, A. Mangini, F. Montanari, and R. Passerini, Gazz. chim. ital., 85, 769, 1955.
19. H. Schubert and H. P. Baumann, Z. Phys. Chem., 203, 351, 1954.
20. V. I. Minkin, O. A. Osipov, V. A. Kogan, R. R. Shagidullin, R. A. Terent'eva, and O. L. Raevskii, ZhFKh, 38, 1718, 1964.
21. H. Kofod, L. E. Sutton, and J. Jackson, J. Chem. Soc., 1467, 1952.
22. O. A. Osipov, V. I. Minkin, and Yu. B. Kletenik, Dipole Moments Manual [in Russian], Rostov-on-Don State University Press, 1961.
23. Heterocyclic Compounds [Russian translation], IL, Moscow, 5, 1961.
24. R. Forsyth and F. Pymann, J. Chem. Soc., 397, 1930.
25. S. A. Hiller, I. B. Mazheika, and I. I. Grandberg, KhGS [Chemistry of Heterocyclic Compounds], p. 107, 1965.

27 February 1965

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