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COMPARATIVE ANALYSIS OF THE ELECTRONIC STRUCTURE OF POSITIONAL ISOMERS: INDOLE—ISOINDOLE

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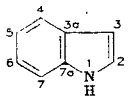
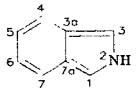
On the basis of an analysis of the canonical and localized molecular orbitals of indole and isoindole, calculated in the SCF and CNDO/2 approximations, as well as an x-ray crystallographic investigation of 2-methyl-isoindole, a comparison of the electronic structure of the positional isomers was made. The 10π-electronic system of isoindole is more integral than for indole: isoindole is a single 10π-electronic system with an appreciable localization of the bonds in the carbocyclic portion of the bicycle; the electronic structure of indole can be represented in a first approximation as the aggregate of three weakly interacting π-subsystems: the benzene ring, the double bond between the α- and β-carbon atoms, and the free electron pair of the nitrogen atom.

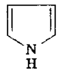
The electronic structure of indole (I) and isoindole (II) has been the subject of several investigations, in which methods of quantum chemistry were used to study the differences in the ground state [1-4], peculiarities of the reactivity [5, 6], and photophysical properties [3, 7, 8]. Despite the existence of a number of studies, there is no unanimity on the electronic structure and factors determining the stability of systems I and II [9].



I



II



III

In all the theoretical investigations conducted until recently, conclusions concerning the differences in the ground state of the structures I and II were drawn on the basis of an analysis of the basis of the canonical molecular orbitals (MO), the properties of the symmetry of which determine their substantial delocalization, which hinders a comparison of the characteristics of individual chemical bonds in related structures.

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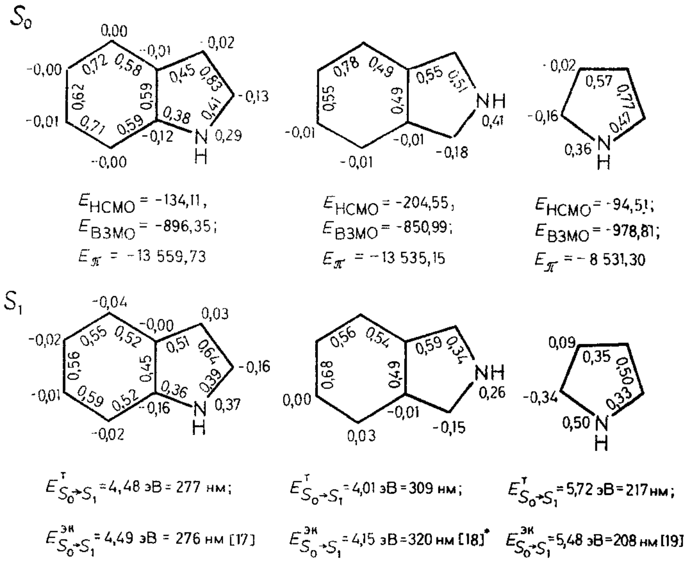

Fig. 1. Data obtained from calculations by the SCF method: π-charges and bond orders in the ground state (S_0) and first excited state (S_1); energies of the LUMO, HOMO, π-electronic energy of the ground state (E)† in kJ/mole, energy of the transition $S_0 \to S_1$ (the experimental value is indicated for comparison).

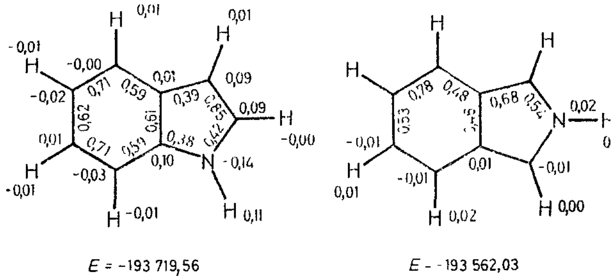

Fig. 2. Data obtained from calculations by the CNDO/2 method: (σ + π) charges, orders of the π-bonds, total energy of electrons in kJ/mole.

In this work, on the basis of a consideration α not only of the canonical but also of the localized MO, we investigated the nature of the chemical bonds in indole and isoindole, and the conclusions of the calculations were confirmed by the results of x-ray crystallographic analysis of single crystals of 2-methylisoindole (IV).

Quantum chemical calculations were performed in the π-approximation by the Pariser-Parr-Pople method [10] and in the CNDO/2 approximation with standard parametrization [11, 12]. The geometrical parameters of the pyrrole molecule III were taken from [13], and for the remaining molecules from studies of related compounds [14, 15].

The data of a calculation of the distribution of charges, bond orders, energies of the lowest unoccupied and highest occupied MO (LUMO and HOMO) by the SCF method, as well as the values of the total π-electronic energies of the isomeric systems and pyrrole, are presented in Fig. 1. Figure 2 presents the results of a calculation of the electronic structure of the isomeric systems by the CNDO/2 method. An analysis of the bond orders $p_{r,s}$ (Fig. 1) shows that in the carbocyclic portion of indole their values are equalized to a greater degree than in isoindole (compare p_{3-3a} and p_{2-3}). This conclusion is well confirmed by the values of the multiplicities of the π-bonds, obtained by the CNDO/2 method (see Fig. 2).

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*Center of the dipole band, possessing a fine structure.

†E_π of benzene = −7448.26 kJ/mole.

A measure of the participation of the heteroatom in conjugation can be estimated, in particular, according to the distribution of electron density on the atoms, and judging by the data of calculations by the two methods (see Figs. 1, 2), it can be asserted that the free electron pair of the nitrogen atom in the case of the isoindole molecule participates more effectively in conjugation with the remainder of the system than in the case of the indole and even pyrrole molecule. Data on the distribution of π-electron density on the atoms, on the basis of the concept of the π-excess of the heterocycles, permit us to approach its quantitative estimation for pyrrole and its benzologs. According to [16], the average negative charge per carbon atom of the heterocyclic system can be considered as a measure of the π-excess. Thus, according to the results of the calculations, the average effective π-charges, considering all the carbon atoms of indole, isoindole, and pyrrole, are equal to −0.036, −0.053, −0.090, respectively, while on the carbon atoms of the pyrrole portion of the bicycles and pyrrole itself they are −0.070, −0.095, −0.090, respectively. The results cited indicate a larger π-excess of isoindole in comparison with indole, while a comparison of the effective π-charges on the carbon atoms of the pyrrole ring of benzopyrroles and the parent compound indicates a greater π-excess of indole even relative to pyrrole. An analysis of the bond orders and the distribution of charges in the pyrrole portion of the bicycles I and II (Figs. 1 and 2) suggests a greater N-H acidity for isoindole in comparison with indole.

The energy of the HOMO of isoindole (see Fig. 1) is substantially higher than the energy of the corresponding MO of indole, which explains the greater stability of indole derivatives of oxidation in comparison with azoindole derivatives, known from practical experience, as well as the pattern of the variation of their first ionization potentials [1, 9]. The relative arrangement of the HOMO-LUMO levels of the isomeric structures that we obtained explains the experimentally observed appreciable difference in the positions of the first absorption bands in the UV spectrum. The value of the energy of the singlet-singlet transition $S_0 \rightarrow S_1$ that we calculated and the value found experimentally for the molecules under consideration are in good mutual correlation. Figure 1 shows the characteristics of the excited state S_1 of isomeric systems and pyrrole. It can be seen that in indole the bond orders in the benzene ring become even more equalized than in the ground state; in the heterocyclic ring there is also appreciable equalization, although to a lesser degree. In the carbocyclic portion of isoindole, in the case of excitation, the distribution of the bond orders is essentially changed: their equalization occurs in such a way that the greatest order in the S_1 state is possessed by the $C_{(5)}$—$C_{(6)}$ bond. On the contrary, in the heterocyclic ring of isoindole the difference between the multiplicities of the $N_{(2)}$—$C_{(3)}$ and $C_{(3)}$—$C_{(3a)}$, bond is enhanced; however, the difference between the multiplicities of the $C_{(3)}$—$C_{(3a)}$ and $C_{(3a)}$—$C_{(7a)}$ bonds is decreased, i.e., it can be noted that in the case of isoindole the delocalization is increased on the whole. However, for indole this increase is more appreciable. The change in the bond orders during excitation can be illustrated by the broad long-wave absorption band. In isoindole the long-wave band is broader than in indole [9, 20]. This corresponds to our conclusions from the calculations (see Fig. 1), on the fact that in the transition to the first singlet excited state, the bond orders of isoindole change to a greater degree than for indole. The indicated level of delocalization in the systems under discussion is reached in various ways. Figure 3 shows the change in the π-charges on the atoms in the transition $S_0 \rightarrow S_1$. As can be seen from these data, in indole the transition to the first singlet excited state is determined by transfer of electron density from the heteroatom to the α-carbon atoms, and to an equal degree to the 4-position. In isoindole the nature of the first electronic transition is substantially different: transfer of electron density occurs to the heteroatom from the 4(7)-position, as well as from the α-positions, but to a lesser degree. It is interesting that in pyrrole the nature of the electronic transition is associated with transfer of electron density from the heteroatom and the β-positions to the α-positions, i.e., is very close to the nature of the transition (its polarization) in indole and has nothing in common with the excitation of isoindole.

From the standpoint of further refining the electronic structure of the compound under consideration we studied the localized MO. Their analysis can be considered as a criterion of verification of the correctness of the structural formulas I and II. The localization procedure was performed by diagonalization of the density matrix of the molecular fragments under consideration. The intrinsic vectors of the matrix obtained have the sense of valence MO, while the intrinsic values determine the population of the localized MO and their valence activity. The isolation of MO with nonzero valence activity permits a quantitative characterization of the localization using a new index — the valence activity of the fragment [21].

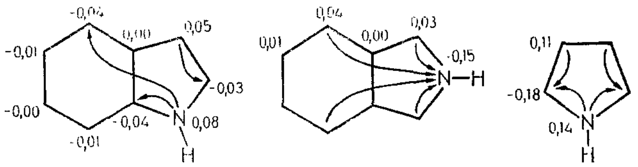


Fig. 3. Change in the electron density on the atoms in the transition from the ground state to the first singlet excited state. The arrows indicate the main directions of displacement of electron density during excitation.

TABLE 1. Valence Activities of Fragments of Molecules of Positional Isomers I and II, Calculated by the SCF Method

Number of atoms contained in the fragment	Valence activities	
	indole (I)	isoindole (II)
1, 2	1,1 (1,13)*	1,1 (1,13)
2, 3	0,6 (0,53)	
3, 3a	1,6 (1,68)	1,1 (1,04)
3a, 7a	1,3 (1,26)	1,5 (1,57)
1, 7a	1,2 (1,19)	
3a, 4	1,3 (1,30)	1,5 (1,54)
4, 5	1,0 (1,00)	0,8 (0,77)
5, 6	1,2 (1,23)	1,4 (1,44)
6, 7	1,0 (1,00)	
7, 7a	1,3 (1,28)	
1, 2, 3	0,6	1,1
1, 2, 7a	1,7	
4, 5, 6, 7	1,0	0,7 (0,71)
2, 3, 3a, 7a	1,3	
1, 2, 3, 3a, 7a	1,0	0,7
3a, 4, 5, 6, 7, 7a	0,6 (0,49)	1,1 (1,22)
1, 3, 3a, 4, 7, 7a	2,2	2,0
1, 7a, 3a, 3		1,3 (1,32)

*The values of the π-components of the valence activities, calculated in the CNDO/2 approximation, are cited in parentheses. In this method, in addition to the atoms indicated in column 1, the hydrogen atoms bonded to them were taken into consideration.

$$V_i = \sum_{j\neq i} P_{ij}^2 = 2P_{ii} - P_{ii}^2,$$

where P_{ij} is an element of the density matrix — the bond orders; P_{ii} is the diagonal element, which has the sense of the population of the i-th orbital.

The method used has been successfully applied to the solution of problems of the electronic structure of coordination compounds with organic ligands [22]. To obtain a more complete idea of the localization in indole and isoindole molecules we investigated the multiplicity of fragments containing from two to six atoms (not considering the hydrogen atoms, which are taken into account in the CNDO/2 method). The valence activities of these fragments are presented in Table 1. A comparison of the π-valence activities of the individual bonds with one another gives an idea of the degree of double bonding of the neighboring atoms: the lower the valence activity of the bond, the greater the localization of π-electrons on it. Analogous considerations are correct for fragments containing a larger number of atoms: the lower the valence activity of the fragment, the more occupied its π-shell. Therefore, an analysis of the valence activity substantiates the possibility of considering the molecules of the investigated compounds in the form of π-subsystems. It is interesting that conclusions on the electronic structure of the compounds under consideration, drawn on the basis of an analysis of the valence activity of two-center fragments, are in good agreement with those obtained on the basis of an analysis of the multiplicities of the bonds: a more or less uniform distribution of electron density is characteristic of the carbocyclic portion of indole and the heterocyclic portion of isoindole. However, judging by the valence

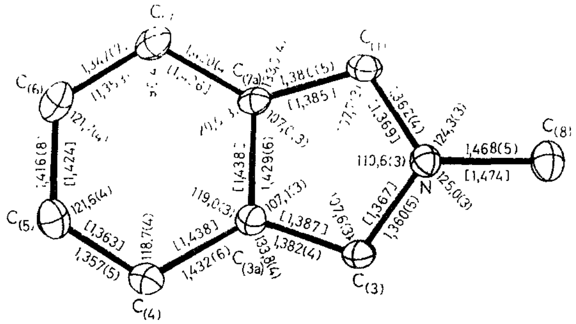
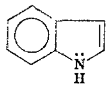
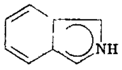


Fig. 4. Data of x-ray crystallographic analysis of N-methylisoindole: general view of the molecule with representation of the atoms by probability ellipsoids of thermal vibrations, bond lengths and valence angles. The bond lengths considering corrections for thermal vibrations of the molecule as a rigid body are indicated in brackets.

activities of the bonds, the π-system of the benzene ring of indole is rather closed (the valence activities of the 3a-7a bond and the remaining bonds of the carbocyclic portion are close; see Table 1), while the π-system of the pyrrole ring of isoindole is not closed (the valence activities of the 1-2 and 3-3a bonds are almost the same but differ appreciably from the valence activity of the 3a-7a bond). Precisely this fact determines the greater internuclear conjugation in isoindole in comparison with indole (see the valence activities of the fragments 3a, 4, 5, 6, 7, and 7a in Table 1). The values of the valence activities of the fragments combining the atoms 4, 5, 6, 7 and 3a, 4, 5, 6, 7, 7a (see Table 1) in isoindole indicates the presence of appreciable localization of the π-electron density on the 4-5 and 6-7 bonds, established earlier, does not mean the absence of conjugation between the indicated fragments and the remainder of the molecule. A comparison of the valence activities of the 4-5 and 5-6 bonds of compound II and the neighboring bonds in s-cis-butadiene (they are equal to 0.2 and 1.8) shows the nonequivalence of the conclusions of [6] on the representation of the structure of isoindole in the form of weakly interacting π-fragments of pyrrole and butadiene. From all the preceding considerations it is understood that our calculations show the inadequacy of the representations of indole and isoindole by the structural representations I and II, respectively. An electronic structure of the compounds under consideration closer to the actual facts can be rendered using structures IA and IIA, which are limiting structures in the sense of localization (the circle and curve within the ring denote more or less uniform distribution of electron density, while each of the lines represents the localization of an electron pair).


IA


IIA

To obtain an objective criterion for verifying the results of calculation according to compound II, we performed an x-ray crystallographic analysis of single crystals of N-methylisoindole as a relatively available compound and the closest to the parent isoindole. Figure 4 shows the general view of the molecule IV with representation of the atoms by probability ellipsoids of the thermal vibrations, bond length and valence angles (for more details on the x-ray crystallographic analysis of compound IV, see [23]). The presence of a flat structure, a comparison of the bond lengths 1-2 with 3-3a, 4-5 with 3a-4 and 5-6, as well as the closeness of the bonds 3a-4 and 3a-7a to aromatic confirm the conclusions of the calculations according to the electronic structure of various fragments and the role of localization-delocalization in the molecule as a whole. The data of x-ray crystallographic analysis of the indole portion of the heteroauxin molecule [15, p. 195] confirm the conclusions drawn with respect to the electronic structure of indole.

Hence, the aforementioned permits us to conclude that there is a substantially different electronic structure of the position isomers. The 10π-electronic system of isoindole is more integral than that of indole: isoindole is a single 10π-electronic system with appreciable localization of the bonds in the carbocyclic portion of the bicycle; the electronic structure of indole can be represented in a first approximation as an aggregate of three weakly interacting π-subssystems: the benzene ring, the double bond between the α- and β-carbon atoms, and the free electron pair of the nitrogen atom.*

Despite the fact that isoindole (II) has a more integral 10π-electronic structure than indole (I), the latter is more stable. In our opinion, this is the result of loss of the quality of the distribution of electron density in the transition from the autonomous 6π-electronic system of the benzene ring in indole to the 10π-electronic system in isoindole, accompanied, moreover, by a definite localization of the bonds in the carbocyclic portion of the molecule. This view of the stability of isoindole differs from those previously accepted [24, 25], explaining the substantial differences as the result of less delocalization of electron density in isoindole in comparison with indole.

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*The latter conclusion should not be accepted categorically, since in the total absence of conjugation between the π-fragments their valence activities would be equal to zero.