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INDOLE DERIVATIVES

137.* QUANTUM-CHEMICAL STUDY OF THE CONFORMATION OF SOME PHENYLHYDRAZONES AND THEIR ENEHYDRAZINE TAUTOMERS

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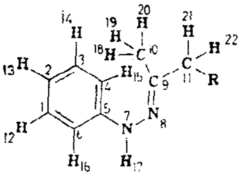
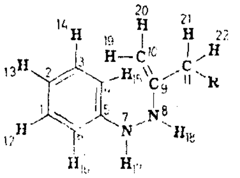
It was shown by the data from quantum-chemical calculations that the phenylhydrazones of certain unsymmetrical carbonyl compounds (methyl ethyl ketone, acetoacetic and levulinic acids) have the transoid conformation in relation to the N—N bond. The relation between the regioselectivity of the Fischer reaction and the structure of the calculated compounds is discussed.

The energy and structure of the possible conformers of the phenylhydrazones of methyl ethyl ketone (I, IV) (R = CH_3), acetoacetic acid (I, IV) (R = COOH), and levulinic acid (I, IV) (R = CH_2COOH) and their enehydrazine tautomers (II, IV, V, VI) were calculated by the AM1 quantum-chemical method [2] in order to determine the most likely conformation of the initial compounds in the Fischer indolization of arylhydrazones. The results are given in the diagram and in Table 1. All the structural and energy indices were obtained as a result of full optimization of the geometry of the investigated molecules.



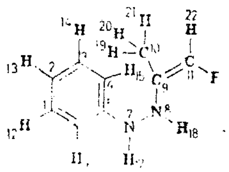
I

$r_{15,18}=2,30$; $r_{15,19}=2,98$; $r_{15,20}=3,93$; $r_{4,10}=3,02$; $r_{6,10}=4,00$; $\theta_{4,5,7,8}=56,6$; $\theta_{5,7,8,9}=8,3$; $\theta_{7,8,9,10}=3,2$; $\theta_{7,8,9,11}=-175,9$



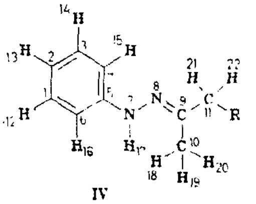
II

$r_{15,19}=4,38$; $r_{15,20}=4,71$; $r_{4,10}=5,44$; $r_{6,10}=6,30$; $\theta_{4,5,7,8}=37,5$; $\theta_{5,7,8,9}==52,7$; $\theta_{7,8,9,10}=39,3$; $\theta_{7,8,9,11}=-146,5$



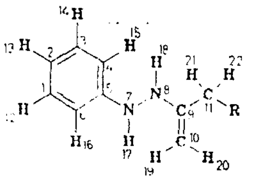
III

$r_{15,19}=5,11$; $r_{15,20}=4,68$; $r_{15,21}=4,21$; $r_{4,10}=5,19$; $r_{6,10}=6,00$; $\theta_{4\ 5,7,8}=39,0$; $\theta_{5,7,8,9}=48,0$; $\theta_{7,8,9,10}=55,9$; $\theta_{7,8,9,10}=-130,4$



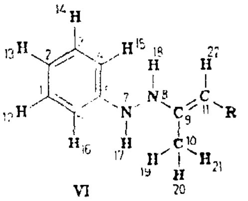
IV

$r_{15,18}=5,80$; $r_{17,18}=3,74$; $\theta_{4,5,7,8}=-0,93$; $\theta_{5,7,8,9}=177,5$; $\theta_{7,8,9,10}=0,68$; $\theta_{7,8,9,11}=-179,2$



V

$r_{15,18}=2,47$; $r_{17,19}=2,40$; $\theta_{4,5,7,8}=-5,88$; $\theta_{5,7,8,9}=-167,9$; $\theta_{7,8,9,10}=-24,2$; $\theta_{7,8,9,11}=160,9$



VI

$r_{15,18}=3,04$; $r_{17,19}=3,05$; $\theta_{4,5,7,8}=-27,9$; $\theta_{5,7,8,9}=153,4$; $\theta_{7,8,9,10}=-46,4$; $\theta_{7,8,9,11}=137,9$

R = CH_3, r — distance between atoms , (Å), θ — dihedral angles

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*For Communication 136, see [1].

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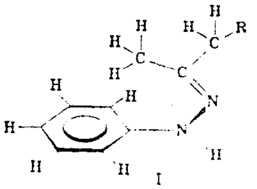
TABLE 1. Total Energies (E) of the Conformers of the Phenylhydrazones and the Enehydrazine Tautomers

Conformer	E, kcal/mole, for		
	$R=CH_3$	$R=COOH$	$R=CH_2COOH$
I	−43554,36	−57730,13	−61327,96
II	−43542,58	−57720,00	−61318,49
III	−43546,27	−57721,59	−61321,52
IV	−43555,05	−57731,06	−61331,65
V	−43535,88	−57717,89	−61319,87
VI	−43540,96	−57721,36	−61322,18

As seen from this diagram, in the phenylhydrazone (I), which has the cisoid conformation in relation to the N—N bond, the enamine fragment of the molecule lies above the benzene ring as a result of rotation about the $C_5—N_7$ bond ($\theta_{4,5,7,8}$ = 56.6°); the atoms at positions 8, 9, 10, and 11 are almost planar ($\theta_{7,8,9,10}$ = 3.2° and $\Theta_{7,8,9,11}$ = −175.9°). In the tautomer (II) the enamine fragment is rotated about the $C_5—N_7$ bond by θ = 37.5° and about the $N^8—C^9$ bond by θ = 39.3°. In the tautomer (III) the angles of rotation about the $C_5—N_7$ and $N_8—C_9$ bonds are 39.0 and 55.9° respectively. The phenylhydrazone (IV) in the transoid conformation in relation to the N—N bond has an almost planar structure. In the enehydrazine tautomer (V) the planarity of the arrangement of the atoms at positions 4, 5, 7, and 8 is slightly disrupted ($\theta_{4,5,7,8}$ = 5.88°), while the enamine fragment is rotated about the $N_8—C_9$ bond by θ = 24.2°. In the tautomer (VI) the planarity is disrupted even more ($\theta_{4,5,7,8}$ = 27.9°), while the angle of rotation about the $N_8—C_9$ bond is 46.4°.

The total energies (E, kcal/mole) of all 18 investigated conformers are given in Table 1. As seen from the data in Table 1, the energetically most favorable is the transoid conformer (IV). In papers devoted to study of the mechanism of Fischer indolization the initial phenylhydrazone is as a rule represented in the cisoid conformation in relation to the N—N bond (e.g., see [3]). This was justified by the inclination to represent the formation of the new bond $C_4—C_{10}$ as the most favorable from the steric standpoint. According to data in [4], this process is realized by an intramolecular [3,3]-sigmatropic rearrangement. As a result of rotation about the N—N bond the stable conformer (IV) is converted into the conformer (I), which can be represented on the basis of the calculated geometric indices in space in the form of the structure presented below, where the imine nitrogen atom lies above the plane of the benzene ring. The above-mentioned [3,3]-sigmatropic rearrangement can probably be realized through the stereochemical structure (I).



I

On the basis of the total energy data (Table 1) the conformers can be arranged in the following order of decreasing stability for all the substituents:

for $R=CH_3$: IV→I→III→II→VI→V
$R=COOH$: IV→I→III→VI→II→V
$R=CH_2COOH$: IV→I→VI→III→V→II

From the presented series it is seen that the stability of the conformer (II) decreases with increase in the size of the substituent, while that of the conformer (VI) increases. Attention is drawn to the fact that the conformer (VI) is more stable than the conformer (V) for all the phenylhydrazones. This means that the tautomeric transformation probably takes place in the (IV) → (VI) direction and not in the (IV) → (V) direction. If the cyclization took place through the tautomer (V), the 2-substituted indole would be obtained as the final product, and if cyclization took place through the tautomer (VI) the 3-substituted 2-methylindole would be obtained. In fact, it has been shown by a series of investigations, e.g., [5,6], that the 3-substituted 2-methylindoles are formed preferentially as a result of the Fischer indolization of the phenylhydrazones of unsymmetrical carbonyl compounds.

Thus, it can be supposed on the basis of the calculations that the phenylhydrazones exist in the transoid conformation in relation to the N—N bond. The order of stability in the investigated tautomers makes it possible to give a qualitative explanation for the experimentally observed regioselectivity in Fischer indolization.

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PROTONATION OF 1,4-BIS(1-VINYL-2-PYRROLYL)BENZENE

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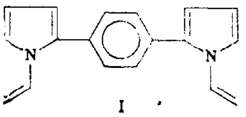
In the reaction of 1,4-bis(1-vinyl-2-pyrrolyl)benzene with hydrogen chloride and hydrogen bromide the hydrogen halide adds at the vinyl groups, and α-protonation takes place in both pyrrole rings. In reaction with the superacidic system HSO_3F + SbF_5 (in SO_2ClF) position 5 of one heterocycle and position 4 of the other are protonated with retention of the vinyl groups.

In molecules containing directly linked five-membered aromatic heterocycles their mutual effect is extremely important. For example, the trifluoroacetylation of 1-vinyl-2-(2-furyl)pyrrole by trifluoroacetic anhydride leads to a mixture of products from acylation at positions 5 of either the pyrrole or the furan rings. Double acylation is not observed [1]. The protonation of furylpyrroles by hydrogen halides also takes place either in the pyrrole ring or in the furan ring but not in both rings at the same time [2]. These facts result from the strong deactivating effect of the partial positive charges that arise at the respective carbon atoms of the nonreacting heterocycle as a result of the formation of a common system of conjugation [3].

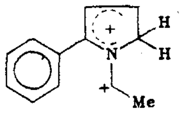
The aim of the present work was to study the mutual effect of N-vinylpyrrole fragments separated by a benzene ring in the case of the protonation of 1,4-bis(1-vinyl-2-pyrrolyl)benzene (I) by the superacidic system HSO_3F + SbF_5 in SO_2ClF and hydrogen halides HCl and HBr. The obtained cations were identified by PMR spectroscopy.



I

On the one hand, the formation of the common system of conjugation can favor ready delocalization of the charge that appears during the protonation of this compound to the most distant atoms in the molecule. On the other hand, the appreciable population of the nonplanar conformations (with respect to the phenyl—heterocycle bonds) [4] should lead to some isolation of the two heterocycles from each other.

It is known that 1-vinyl-2-phenylpyrrole undergoes double protonation at the α position of the ring and the β position of the vinyl group in the HSO_3F + SbF_5 system with the formation of the dication [5]:



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