QUANTUM-CHEMICAL INVESTIGATION OF THE PROTONATED FORMS OF 2-(2-FURYL)PYRROLE

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The electron and conformational structures, as well as the internal rotation, of 2-(2-furyl)pyrrole and its \( \alpha \)-protonated forms were studied by the MNDO method with complete optimization of the geometry. In conformity with the experiments (PMR), the two delocalized cations with a cis orientation of the heteroatoms that are formed as a result of protonation of the pyrrole or furan ring have the greatest and virtually equal stabilities \( (\Delta H = 738.7 \text{ and } 740.6 \text{ kJ/mole}) \).

As the simplest models of conducting polypyrroles and polythiophenes, directly bonded five-membered aromatic heterocycles are currently becoming the subjects of intensive experimental [1-5] and theoretical [6-8] investigations. Of particular interest in this respect is 2-(2-furyl)pyrrole, which models copolymers of pyrrole and furan with increased stability of the conducting properties [9]. An investigation of the electron structures and conformational behavior of the protonated forms of 2-(2-furyl)pyrrole and its analogs is the next logical step toward a better understanding of the mechanisms of both the polymerization of such systems and the electrical conductivity of the resulting polymers.

We have previously shown [10, 11] on the basis of NMR data that equilibrium mixtures of pyrrolium and furanium cations are formed as a result of the protonation of 2-(2-furyl)pyrrole; this constitutes evidence for the successful competition of the directly bonded pyrrole and furan rings in thermodynamically controlled electrophilic processes. This fact is fundamental in light of the well-known relationship of the reactivities of the isolated aromatic five-membered heterocycles: pyrrole >> furan.

The goal of the present research was to conduct a theoretical study of the stabilizing interannular effects and the associated characteristics of the conformational behavior of the protonated forms II and III of 2-(2-furyl)pyrrole (see Fig. 1).

To achieve our goal we used the semiempirical MNDO method. It sufficiently accurately reproduces the heats of formation and the geometrical characteristics vis-à-vis the insignificant, as compared with the nonempirical method, expenditure of computer processor time.

To verify the adequacy of the method the results of our calculations of the geometries and conformational characteristics of 2-(2-furyl)pyrrole were compared with the results of nonempirical calculations of the same compound [8]. Good agreement for the optimized values of the bond lengths and bond angles is observed (see Table 1). The STO-3G and 4-31G bases give substantially different estimates of the difference in the total energies of the cis and trans conformers of 2-(2-furyl)pyrrole (IA and IB): 4.2 and 10.0 kJ/mole, respectively (see Table 2). The MNDO method estimates this value as being 7.1 kJ/mole. The dipole moments of cis-conformer IA obtained by the MNDO method and the nonempirical method in the 4-31G basis have approximately the same scatter with respect to the experimental value.
The most substantial differences are observed when one compares the forms of the potential curves and the barriers to internal rotation (BIR) of 2-(2-furyl)pyrrole relative to the C(2)=C(2') bond (Fig. 2). The barrier to rotation, which is clearly expressed in the STO-3G basis (21.8 kJ/mole), increases in the 4-31G basis to 25.5 kJ/mole, while, according to the results of the MNDO method, the IA → IB transition is realized without a barrier (Fig. 2, curve 3; Table 2). A peculiarity of the MNDO method, which consists in understatement of the barrier to internal rotation (BIR), is well known and has been studied in detail. Fabian [12] links it primarily to overestimating the energies of repulsion between the valence-nonbonded atoms (the hydrogen atoms of adjacent rings in this case). The noted inadequacy requires care in analyzing the potentials of internal rotation by the MNDO method. The data obtained can be examined on a qualitative level or interpreted as an approximate estimate of the barrier to rotation from below.

Reasons for the regiospecificity of the primary protonation of 2-(2-furyl)pyrrole in the C(5) position of the pyrrole ring and subsequent thermodynamically controlled protonation in the C(5) position of the furan ring with partial deprotonation of the pyrrole ring and the formation of an equilibrium (approximately equimolar) mixture of pyrrolium (IIA, IIB) and furanium (IIIA, IIIB) cations were discussed in [11].

An analysis of the experimental data [11], the charge distribution, and the character of the highest occupied molecular orbitals (HOMO) (Fig. 3) confirms the conclusion [11] that primary attack by the proton at the C(5) atom is orbitally controlled. Evidence for this is provided by the greatest contribution of the $p_z$ orbital of this atom (+0.46) to the HOMO. The $p_z$ orbital of the C(2) atom, which is not protonated because of its steric shielding, makes the same (in absolute value) contribution to the HOMO.