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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 α-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 (ΔH = 738.7 and 740.6 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.

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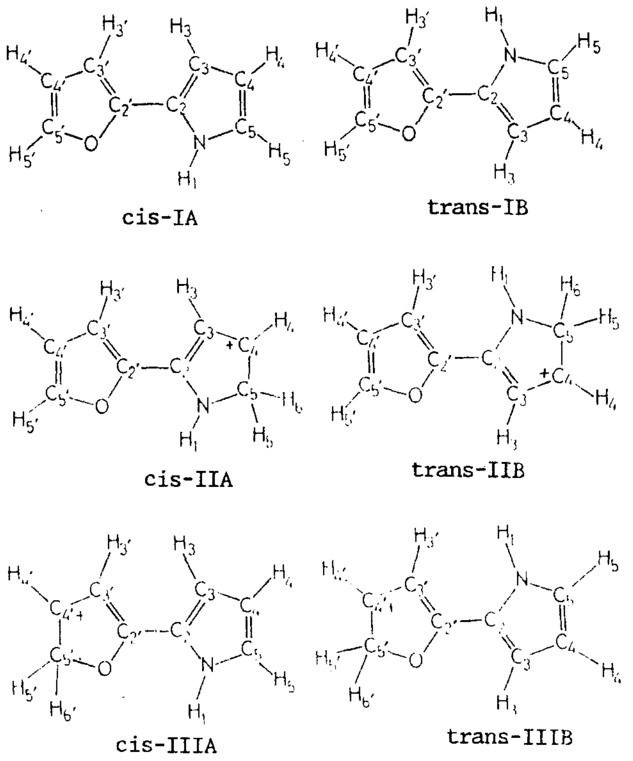
cis-IA trans-IB

cis-IIA trans-IIB

cis-IIIA trans-IIIB

Fig. 1. Conformers of 2-(2-furyl)pyrrole (IA, IB) and its protonated forms (IIA, IIB, IIIA, IIIB).

TABLE 1. Results of Optimization of Some Geometrical Parameters of 2-(2-Furyl)pyrrole by the MNDO and ab initio Methods

Bond	R, Å		Angle	φ°	
	MNDO	STO-3G		MNDO	STO-3G
$C_{(2)}—C_{(2')}$	1,45	1,47	$N—C_{(2)}—C_{(2')}$	123,4	121,1
$H_{(1)}—O$	2,74	2,55	$O—C_{(2')}—C_{(2)}$	118,8	116,9

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.

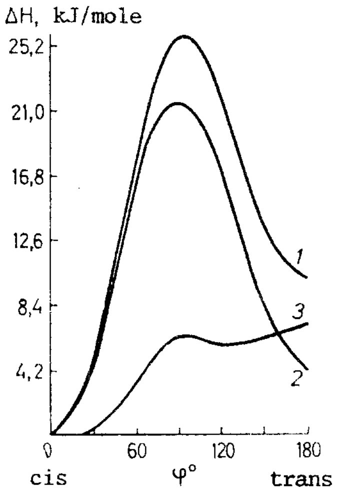

Fig. 2

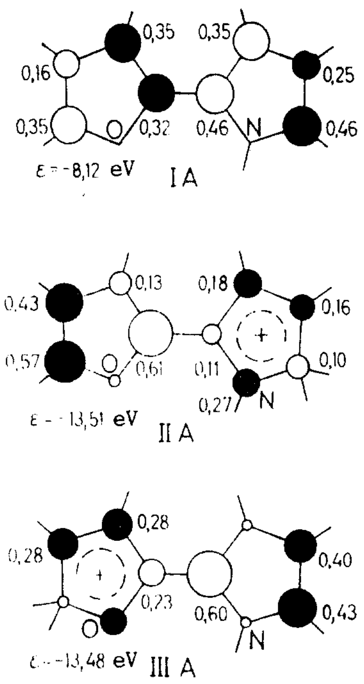

Fig. 3

Fig. 2. Potential curves of the internal rotation of 2-(2-furyl)pyrrole according to data obtained by the ab initio [4-31G (1) and STO-3G (2)] [8] and MNDO (3) methods.

Fig. 3. Structures of the HOMO of the *cis* conformers of 2-(2-furyl)pyrrole (IA) and its protonated forms (IIA, IIIA).

TABLE 2. Some Calculated (MNDO and ab initio) and Experimental Characteristics of 2-(2-Furyl)pyrrole

Method	ΔH (cis/trans), kJ/mole	Barrier h [$C_{(2)}$-$C_{(2')}$], kJ/mole	μ_{cis}, D
STO-3G [8]	4,2	21,8	—
4-31G [8]	10,0	25,5	1,04
MNDO	7,1	0,0	1,58
Expt.	—	—	1,33

As has already been noted [11], the calculated heats of formation of the planar forms (*cis* and *trans*) of pyrrolium and furanium cations (see Table 3) unexpectedly coincided with great accuracy, which attests to the identical stabilities of structures IIA and IIIA (IIB and IIIB, respectively). Considering the much greater protophilicity of the isolated pyrrole ring as compared with the furan ring one might assume that, being linked together, they manifest a substantially different (in strength) mutual stabilizing ability with respect to the cation formed in one of the rings due to the addition of a proton.

This fact deserves a great deal of attention, since it is a manifestation of a common mechanism of conductivity of an effect and stabilization in the protonated forms of compounds with conjugated heteroaromatic groups with different natures, also including similarly constructed polymeric systems. Having in mind an elucidation of the details of this mechanism, as well as an evaluation of the intensity of the mutual effect of the pyrrole and furan rings in the case of alternate protonation, we used the MNDO method to carry out detailed calculations of the conformers of 2-(2-furyl)pyrrole and its protonated forms with construction of the potentials of internal rotation; in all cases we completely optimized the geometrical parameters of the calculated systems.

An appreciable change in the principal geometrical characteristics of the 2-(2-furyl)pyrrole molecule occurs as a result of protonation (see Table 4). The length of the bond between the rings and the geometry of the protonated ring change most substantially. The length of the $C_{(2)}$—$C_{(2')}$ bond (1.45 Å in the unprotonated IA molecule) decreases

TABLE 3. Heats of Formation of the Conformers of 2-(2-Furyl)pyrrole and Protonated Forms

Structure	ΔH, kJ/mole		
	I	II	III
cis (A)	87,32	738,73	740,57
trans (B)	94,22	745,80	748,60
gauche(ϕ = 90°)	93,39	776,80	829,39

TABLE 4. Principal Geometrical Parameters of the *cis* Conformers of 2-(2-Furyl)-pyrrole and Its Protonated Forms According to Data Obtained by the MNDO Method

Bond	R, Å			Angle	φ°		
	IA	IIA	IIIA		IA	IIA	IIIA
$C_{(2)}—C_{(2')}$	1,45	1,43	1,40	$N—C_{(2)}—C_{(2')}$	123,4	125,6	124,6
$N—C_{(2)}$	1,40	1,36	1,43	$O—C_{(2')}—C_{(2)}$	118,8	119,4	120,9
$C_{(2)}—C_{(3)}$	1,41	1,48	1,45	$N—C_{(2)}—C_{(3)}$	106,6	106,2	105,1
$C_{(3)}—C_{(4)}$	1,43	1,36	1,40	$C_{(2)}—C_{(3)}—C_{(4)}$	108,2	109,1	108,4
$C_{(4)}—C_{(5)}$	1,40	1,52	1,44	$C_{(3)}—C_{(4)}—C_{(5)}$	107,5	110,0	107,8
$C_{(5)}—N$	1,39	1,49	1,36	$C_{(4)}—C_{(5)}—N$	107,7	101,3	108,3
$O—C_{(2')}$	1,38	1,39	1,35	$C_{(5)}—N—C_{(2)}$	110,0	112,7	110,5
$C_{(2')}—C_{(3')}$	1,40	1,42	1,48	$O—C_{(2')}—C_{(3')}$	109,2	108,5	109,1
$C_{(3')}—C_{(4')}$	1,44	1,42	1,36	$C_{(2')}—C_{(3')}—C_{(4')}$	106,4	106,5	107,4
$C_{(4')}—C_{(5')}$	1,39	1,41	1,52	$C_{(3')}—C_{(4')}—C_{(5')}$	105,9	106,1	108,6
$C_{(5)}—O$	1,37	1,35	1,44	$C_{(4')}—C_{(5')}—O$	110,4	110,6	103,9
$N—H$	0,99	1,00	1,00	$C_{(5')}—O—C_{(2')}$	108,1	108,3	110,9
$C_R—H$*	1,08	1,08	1,08				
$C_{(5)}—H$ ($C_{(5')}—H$)		1,12	1,12				

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*Ring C—H bonds.

to 1.43 Å in the case of protonation of the pyrrole ring (IIA) and to 1.40 Å in the case of protonation of the furan ring (IIIA). In the protonated ring the $C_{(2)}—C_{(3)}$ [$C_{(2')}—C_{(3')}$] and $C_{(4)}—C_{(5)}$ [$C_{(4')}—C_{(5')}$] bonds become longer, the $C_{(3)}—C_{(4)}$ [$C_{(3')}—C_{(4')}$] bond becomes shorter, and angle $C_{(4)}—C_{(5)}—N$ [$C_{(4')}—C_{(5')}—O$] decreases. It is interesting that the changes that occur in one of the rings have virtually no effect on the adjacent unprotonated ring. The two protonated forms of the furylpyrrole, both the *cis* (IIA and IIIA) and the *trans* (IIB and IIIB) conformers, are planar molecules, while the unprotonated molecule (IA) is characterized by an angle of 12.7° between the planes of the pyrrole and furan rings (calculation with complete optimization of the geometry). The observed pattern of the change in the geometrical parameters of the furylpyrrole in the case of protonation corresponds to an increase in the interannular conjugation, which stabilizes the resulting cations.

A change in the symmetry of the HOMO of the furylpyrrole upon protonation also attests to an increase in the $\pi—\pi$ conjugation between the rings in the protonated forms. Whereas in the neutral molecule (IA, Fig. 3) the HOMO is an antibonding orbital with respect to the $C_{(2)}—C_{(2')}$ bond between the rings [the p_z orbitals of the $C_{(2)}$ and $C_{(2')}$ atoms make contributions with different signs], in the molecules of the protonated forms (IIA and IIIA, Fig. 3) it becomes a bonding orbital, which facilitates the transfer of electron density from one ring to the other. The increase in the electron density on the $C_{(2)}—C_{(2')}$ bond corresponds to an increase in its order (see Table 5).

Delocalization of the positive charge via donation of electron density by the unprotonated ring to the adjacent protonated ring and the resulting increasing conjugation are quite apparent in the case of distribution of the π charges on the atoms in the protonated forms of the furylpyrrole. In the IIA structure with a protonated pyrrole ring transfer of π-electron density from the furan ring to the pyrrole ring leads to polarization of the $C_{(2)}—C_{(2')}$ bond [the π charges on the $C_{(2)}$ and $C_{(2')}$ atoms are 0.29 and −0.28, respectively], as well as to a decrease in the π charges on the $C_{(3)}$ and

TABLE 5. Principal Parameters That Characterize the Conjugation Between the Pyrrole and Furan Rings in 2-(2-Furyl)pyrrole (IA) and Its Protonated Forms (IIA, IIIA)*

Structure	Bond order	R, Å	Barrier h, kJ/mole	V_2, kJ/mole
IA	1,02	1,45	0,00	2,51
IIA	1,17	1,43	31,05	34,39
IIIA	1,38	1,40	80,84	85,48

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*The corresponding *trans* conformers (structures IB-IIIB) have close values of the parameters presented.

$C_{(5)}$ atoms of the furan ring to 0.15 and 0.14. Correspondingly, the positive charges in the $C_{(4)}$ and $C_{(5)}$ positions of the pyrrole ring are only 0.15 and 0.01. A small increase in the positive charge on virtually all of the hydrogen atoms is also observed. A similar pattern of the charge distribution occurs in the structure with a protonated furan ring (see Table 6). On the whole, as shown in [11], the positive charge is distributed rather uniformly over the entire molecule, which also ensures the stability of the corresponding cation.

The previously investigated ^{13}C NMR chemical shifts of protonated (in the pyrrole ring) 1-vinyl-2-methyl-, 1-vinyl-2-phenyl-, and 1-vinyl-2-(2-furyl)pyrrole are also in agreement with this analysis. The changes in the $C_{(2)}$ and $C_{(2')}$ shifts on protonation are as follows:

Substituent	$\Delta C_{(2)}$	$\Delta C_{(2')}$
2-Methyl	54,3	—
2-Phenyl	44,1	−6,8
2-(2-Furyl)	33,1	−4,0

The smallest degree of deshielding of $C_{(2)}$ [and shielding of $C_{(2')}$] corresponds to the greatest degree (for this series) of transfer of π-electron density to the protonated pyrrole ring. The differences in the shifts of the $C_{(2)}$ and $C_{(2')}$ atoms, which characterize the polarization of the interannular bond, are 0.2 ppm and 21.1 ppm, respectively, for 2-phenyl-1-vinylpyrrole and its cation, as compared with −19.5 ppm and 14.6 ppm, respectively, for 2-(2-furyl)-substituted compounds [13], i.e., even the sign of the polarization changes in this case.

It is evident that to shed some light on the question of the strength of the stabilizing effect of the pyrrole and furan rings with respect to the corresponding cation it is necessary to evaluate by some method the energies of protonated forms IIA and IIIA (IIB and IIIB) in the absence of conjugation. For this we calculated the potential curves of the internal rotation of the two protonated forms relative to the $C_{(2)}—C_{(2')}$ bond (Fig. 4). Angle φ was varied from 0° to 180° in 30° intervals. Additional optimization of the geometrical parameters was carried out at all points. It follows from the orientation of the p_z atomic orbitals that conjugation between the pyrrole and furan rings is minimal in the vicinity of the point $\varphi = 90°$. In other words, the heights of the barriers to internal rotation (BIR) of the two protonated forms of the furylpyrrole can serve as an approximate estimate of the increases in their total energies in the case of a "disconnected" interaction between the pyrrole and furan rings. According to the data in Table 5, the height of the BIR of the isomer with a protonated furan ring is greater by a factor of ~2.5 than the height of the BIR of the molecule with a protonated pyrrole ring (80.8 and 31.1 kJ/mole, respectively). Proceeding from the results of estimation of the BIR of the unprotonated form by the MNDO method and regarding these data as an estimate of the barrier from below, one may assume that the higher BIR actually correspond to the protonated forms. Taking into account the fact that the BIR also depend on the steric repulsion of the interacting groups, the orientation of their dipole moments, and other factors, the rotation potentials obtained were expanded into a six-membered Fourier series to refine the contribution of $\pi—\pi$ conjugation:

$$\Delta E = E(\varphi) - E(0) = \sum_{i=1}^{6} {}^1\!/\!_2 V_i [1 - \cos(i\varphi)].$$

According to [14, 15], π conjugation is characterized by coefficient of expansion V_2. Precisely this term dominates in the expansion of the rotation potentials of the protonated forms of the furylpyrrole (see Table 7). In addition, the V_2 coefficient of the isomer with a protonated furan ring (IIIA) is greater by a factor of 2.5 than for the isomer with a protonated pyrrole ring (IIA), which is in good agreement with the previously found relationships between the BIR of these compounds.

TABLE 6. Distribution of the Charges* in Various Conformations of 2-(2-Furyl)pyrrole and Its Protonated Forms

Atom	Distribution of the charges (π charges)								
	syn	anti	90°	syn	anti	90°	syn	anti	90°
	2-(2-Furyl)pyrrole			Protonated pyrrole ring			Protonated furan ring		
N	−0,20 (0,38)	−0,20 (0,37)	−0,20 (0,33)	−0,27 (0,39)	−0,28 (0,38)	−0,23 (0,47)	−0,16 (0,45)	−0,17 (0,43)	−0,15 (0,42)
C_2	0,01 (−0,13)	0,00 (−0,14)	0,00 (−0,14)	0,36 (0,29)	0,36 (0,29)	0,41 (0,37)	−0,14 (−0,26)	−0,15 (−0,26)	−0,29 (−0,41)
C_3	−0,10 (−0,07)	−0,08 (−0,05)	−0,08 (=0,05)	−0,13 (−0,08)	−0,12 (−0,06)	−0,13 (−0,06)	0,09 (0,14)	0,11 (0,16)	0,05 (0,06)
C_4	−0,14 (−0,10)	−0,14 (−0,10)	−0,14 (−0,10)	0,01 (0,15)	0,00 (0,14)	0,03 (0,16)	−0,15 (−0,09)	−0,16 (−0,09)	−0,14 (−0,09)
C_5	−0,01 (−0,07)	−0,09 (−0,07)	−0,01 (−0,07)	0,13 (0,01)	0,14 (0,01)	0,12 (0,00)	0,19 (0,19)	0,19 (0,19)	0,09 (0,06)
H_1	0,21	0,20	0,20	0,25	0,24	0,25	0,24	0,23	0,22
H_3	0,08	0,09	0,08	0,13	0,14	0,14	0,11	0,12	0,10
H_4	0,08	0,08	0,08	0,13	0,13	0,14	0,13	0,13	0,12
H_5	0,10	0,10	0,09	0,09	0,09	0,10	0,14	0,14	0,13
O	−0,14 (0,28)	−0,11 (0,27)	−0,12	−0,11 (0,28)	−0,08 (0,29)	−0,09 (0,64)	−0,22 (0,21)	−0,20 (0,21)	−0,14 (0,59)
$C_{2'}$	0,04 (−0,06)	0,05 (−0,07)	0,03 (0,19)	−0,17 (−0,28)	−0,16 (−0,27)	−0,22 (0,16)	0,33 (0,27)	0,33 (0,27)	0,50 (0,19)
$C_{3'}$	−0,11 (−0,06)	−0,13 (−0,09)	−0,10 (0,07)	0,09 (0,15)	0,07 (0,13)	0,03 (−0,07)	−0,14 (−0,08)	−0,16 (−0,09)	−0,17 (0,03)
$C_{4'}$	−0,13 (−0,07)	−0,13 (−0,08)	−0,14 (0,09)	−0,16 (=0,08)	−0,16 (−0,08)	−0,14 (−0,10)	0,00 (0,15)	0,01 (0,16)	0,05 (0,06)
$C_{5'}$	−0,01 (−0,05)	−0,08 (−0,06)	0,00 (0,07)	0,16 (0,14)	0,16 (0,14)	0,10 (−0,05)	0,14 (0,00)	0,13 (0,00)	0,10 (0,08)
$H_{3'}$	0,09	0,08	0,09	0,12	0,11	0,11	0,13	0,12	0,16
$H_{4'}$	0,09	0,10	0,09	0,13	0,13	0,13	0,14	0,13	0,15
$H_{5'}$	0,12	0,12	0,12	0,16	0,16	0,15	0,09	0,09	0,12

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*The π charges are given in parentheses.

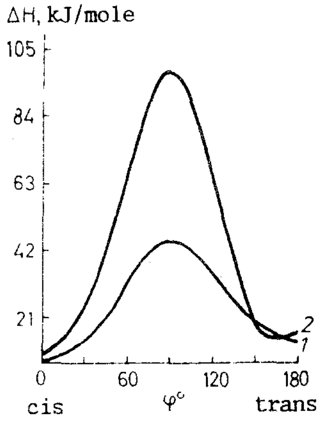

Fig. 4. Potential curves of the internal rotation of protonated 2-(2-furyl)pyrrole: 1) protonation in the pyrrole ring; 2) protonation in the furan ring. Curves 1 and 2 were constructed by means of a computer using the coefficients of expansion into a Fourier series of the potentials of internal rotation (Table 7).

TABLE 7. Approximation by a Fourier Series of the Potentials of Internal Rotation of 2-(2-Furyl)-pyrrole and Its Protonated Forms

Structure	V_1	V_2	V_3	V_4	V_5	V_6
IA	6,53	2,51	0,71	−1,09	−0,08	0,08
IIA	7,49	34,39	−0,46	−3,18	0,00	0,17
IIIA	2,85	85,48	0,21	−14,27	4,98	−4,81

The results obtained constitute evidence that the BIR of the protonated forms of the furylpyrrole observed within the framework of the MNDO method are virtually completely due to the presence of π—π conjugation, the foundation of which is the donation of π-electron density of the unprotonated ring to the adjacent protonated ring, which leads to stabilization of the system as a whole due to delocalization of the positive charge and the formation of a π bond between the rings. The heights of the BIR are proportional to the effectiveness of the π—π conjugation and, consequently, to the capacity for donation of π-electron density by the unprotonated part of the molecule. Thus the stabilizing capacity of the pyrrole ring with respect to the protonated furan ring (cations IIIA and IIIB) is higher by a factor of ~2.5 than the stabilizing capacity of the furan ring with respect to the protonated pyrrole ring (cations IIA and IIB). The more pronounced conjugation in cations IIIA and IIIB as compared with cations IIA and IIB is also manifested in the shorter length of the $C_{(2)}$—$C_{(2')}$ bond and its higher order in the former as compared with the latter (see Table 5).

The absence, according to the results of the MNDO method, of BIR in the unprotonated furylpyrrole is associated with the domination of the V_1 coefficient in the Fourier expansion for the rotation potential (see Table 7). In conformity with [14, 15], this coefficient conveys information regarding the strength of the steric and electrostatic interactions between the rotating groups. Thus the result obtained once again confirms the data in [12] regarding the overestimation of the energies of repulsion between nonbonded atoms by the MNDO method.

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LACTAM AND ACID AMIDE ACETALS

68.* 1-CYANOMETHYL-2-PYRROLIDONE DIETHYLACETAL IN THE SYNTHESIS OF 7,8-TRIMETHYLENEPURINE DERIVATIVES

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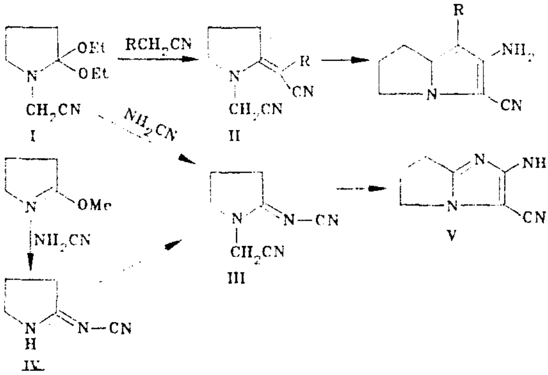
1-Cyanomethyl-2-cyaniminopyrrolidine was synthesized by the reaction of 1-cyanomethyl-2-pyrrolidone diethylacetal with cyanamide. The product undergoes Thorpe—Ziegler cyclization under the influence of sodium ethoxide to give 2-amino-3-cyano-5,6-dihydro-7H-pyrrolo[1,2-a]imidazole, from which 4-amino derivatives of pyrrolo[2,1-f]purine were synthesized.

This research continues studies of the intramolecular Thorpe—Ziegler cyclization of various synthones obtained from 1-cyanomethyl-2-pyrrolidone diethylacetal (I). It has been previously shown that acetal I reacts smoothly with various CH acids such as cyanoacetic esters and malonodinitrile to give enamino nitriles II, which are capable, under the influence of bases, of undergoing cyclization to 5-cyano-6-aminopyrrolizine derivatives [2]. The latter were used for the synthesis of the first representatives of two new heterocyclic systems — pyrimido[5,4-*e*]- and pyrimido[4,5-*f*]pyrrolizine derivatives [3, 4].

The present paper is devoted to the study of a similar scheme but with N-cyano amidines III, rather than enamino nitriles of the II type, as the starting compounds.



Amidines III are readily synthesized by the reaction of acetal I with cyanamide — the reaction proceeds smoothly and gives the products in virtually quantitative yields. Since the N-alkylation of cyano amidines that contain

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*See [1] for Communication 67.

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