77. M. O. Gorbunova, L. N. Faleeva, I. E. Uflyand (Ufland), Yu. I. Ryabukhin, and V. N. Sheinker, in: Abstracts of Papers Presented at the Symposium on the Chemistry of Heterocyclic Compounds (8th) and of Nucleic Acid Components (6th). Nucleic Acids Symposia Series, IRL Press Limited, Oxford, England (1984), No. 14, p. 171.
78. Yu. I. Ryabukhin, L. N. Faleeva, and G. N. Dorofeenko, *Khim. Geterotsikl. Soedin.*, No. 10, 1423 (1981).
79. H. Masachi and I. Toshikazu, *Chem. Lett.*, 5, 499 (1975).
80. K. T. Potts and I. Marshall, *J. Org. Chem.*, 44, 626 (1979).
81. K. T. Potts and I. Marshall, *J. Chem. Soc., Chem. Commun.*, No. 17, 1000 (1972).
82. W. Friedrichsen, W.-O. Schröher, and T. Debaerdemaeker, *Liebigs Ann. Chem.*, No. 11, 1850 (1980).

AMIDINE TAUTOMERISM IN THE 1,3-DIACYL-2-(5-SUBSTITUTED FURFURYL)THIOUREA SERIES. MOLECULAR STRUCTURE OF 1,3-DIACETYL-2-(5-ETHOXYCARBONYLFURFURYL)THIOUREA

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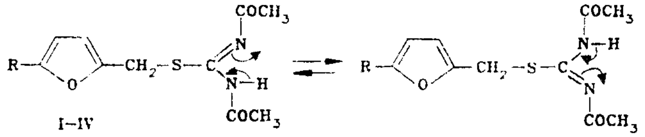
The effect of substituents in the furan ring on the dynamics of amidine tautomerism in 1,3-diacetyl-2-(5-R-furfuryl)thioureas is demonstrated. The conformation of 1,3-diacetyl-2-(5-ethoxycarbonylfurfuryl)thiourea was established by x-ray diffraction analysis.

It is known that the mechanism, rate, and thermodynamic parameters of amidine tautomerism depend on the concentration, the nature of the solvent, the character of the substituents attached to the nitrogen and carbon atoms of the N—C=N fragment, and a number of other factors such as, for example, the acid—base equilibrium in the case of prototropic tautomerism (for example, see [1-6]).

In the present paper we present the facts of the effect of substituents attached to the $C_{(2)}$ atom of the amidine fragment of the 1,3-diacetyl-2-furfurylthiourea I-IV molecules on amidine tautomerism.



I R=$COOC_2H_5$; II R=NO_2; III R=CN; IV R=CHO

According to our data [7], only one set of signals corresponding to the protons of acyl groups is observed in the PMR spectra of II and its analogs (1,3-dipropionyl and 1,3-dibenzoyl derivatives) at room temperature; this is evidently the result of the rather fast (on the NMR time scale) exchange of a proton between the nitrogen atoms of the amido and imido groups. At −70°C the PMR spectra of dilute (≈0.05 mole/liter) solutions contain two distinctly resolved singlets of equal intensities of the protons of acetyl groups and a relatively narrow singlet of an NH proton at ≈12 ppm (Table 1); according to [3], this attests to slow exchange of the NH proton. The position of the signal of the NH proton indicates the possibility of the formation of an intramolecular hydrogen bond (IMHB). Raising the temperature leads to broadening and then to coalescence of the signals of the methyl groups. The coalescence temperature and, consequently, the energy barrier to exchange depend on the character of the substituent in the furan ring (see Table 1).

Transmission of the electronic properties of the substituents in I-IV should take place through the CH_2—S grouping, which is not a good conductor of these effects. The manifestation of a field effect and/or a dipole-dipole interaction between polar groups in the I-IV molecules should be associated with the realization of a certain

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TABLE 1. PMR Spectra and Some Kinetic and Activation Parameters of the Amidine Tautomerism of I-IV

Compound	δ, ppm (J, Hz)*							δν, Hz**	T_{coal}, °K	k_{coal}, sec^{-1}	$\Delta G^{\neq}$, kJ/mole***
	N—H	3-H	4-H	J_{34}	CH_2S	CH_3CO	R				
I	12,12	6,53	7,15	4,0	4.38	2,21	4,30 (q, 2H); 1,32 (t, 3H, J=7,6)	6,3	304	14,0	60,3
II	12,10	6,75	7,47	4,0	4,37	2,18		5,9	274	13,0	54,5
III	12,05	6,62	7,37	4,0	4,37	2,22		5,8	225	12,9	44,7
IV	12,08	6,63	7,35	4,0	4,39	2,20	9,56	6,0	213	13,3	42,2

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*When $T > T_{coal}$.

**The difference between the chemical shifts of the amide and imide acetyl groups when T = 203°K

***When $T = T_{coal}$.

TABLE 2. Coordinates of the Atoms (·10^4; ·10^3 for the H Atoms) of the I Molecule

Atom	x	y	z	Atom	x	y	z
S	7803(1)	4270(1)	4998(1)	$C_{(11)}$	4411(2)	1934(3)	3036(2)
$O_{(1)}$	9394(1)	1321(2)	6862(1)	$C_{(12)}$	3461(2)	−79(3)	2480(2)
$O_{(2)}$	11301(2)	4214(2)	1954(2)	$C_{(13)}$	3511(2)	−782(4)	1280(3)
$O_{(3)}$	5493(1)	3972(1)	3437(1)	$H_{(1)}$	1091(3)	283(4)	404(8)
$O_{(4)}$	3783(1)	1710(2)	4175(2)	$H_{(31)}$	1168(8)	−27(9)	734(5)
$O_{(5)}$	4359(1)	1129(2)	2090(1)	$H_{(32)}$	1224(3)	65(1)	597(7)
$N_{(1)}$	10249(1)	2805(2)	4613(2)	$H_{(33)}$	1184(1)	−57(7)	571(2)
$N_{(2)}$	9263(1)	5466(2)	2622(2)	$H_{(51)}$	1094(1)	707(1)	−23(7)
$C_{(1)}$	9225(2)	4191(2)	3950(2)	$H_{(52)}$	1017(1)	831(1)	67(2)
$C_{(2)}$	10300(2)	1417(3)	6027(2)	$H_{(53)}$	953(3)	745(1)	−11(5)
$C_{(3)}$	11553(2)	92(3)	6418(2)	$H_{(61)}$	589(2)	648(5)	410(4)
$C_{(4)}$	10354(2)	5483(3)	1726(2)	$H_{(62)}$	718(1)	689(2)	296(8)
$C_{(5)}$	10264(2)	7269(3)	375(2)	$H_{(8)}$	726(6)	558(8)	73(2)
$C_{(6)}$	6740(2)	6005(3)	3574(2)	$H_{(9)}$	607(3)	332(8)	45(3)
$C_{(7)}$	6345(2)	5060(2)	2725(2)	$H_{(121)}$	372(5)	−114(4)	345(3)
$C_{(8)}$	6693(2)	4939(3)	1396(2)	$H_{(122)}$	262(7)	71(6)	258(7)
$C_{(9)}$	6033(2)	3683(3)	1265(2)	$H_{(131)}$	325(1)	35(1)	37(1)
$C_{(10)}$	5316(2)	3135(3)	2513(2)	$H_{(132)}$	432(7)	−143(6)	108(8)
				$H_{(133)}$	291(8)	−169(2)	146(3)

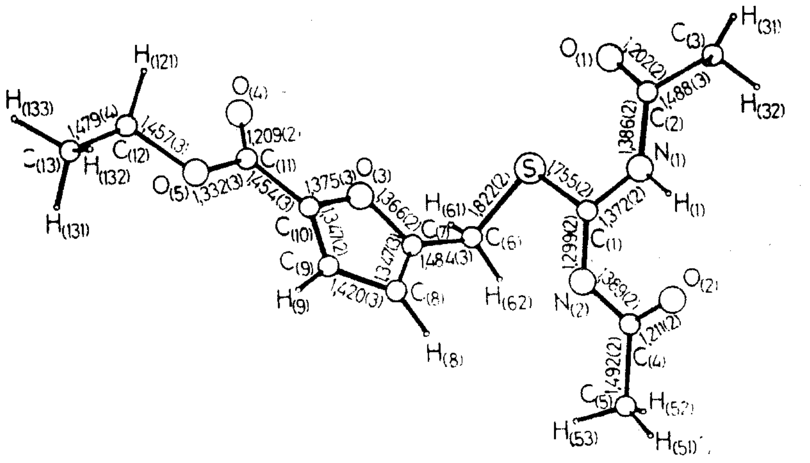

Fig. 1. Projection of the three-dimensional model of the I molecule.

TABLE 3. Bond Angles in the I Structure

Atoms	ω°	Atoms	ω°
$C_{(1)}—S—C_{(6)}$	99,9(1)	$C_{(7)}—O_{(3)}—C_{(10)}$	106,5(1)
$C_{(11)}O_{(5)}—C_{(12)}$	116,1(2)	$C_{(1)}—N_{(1)}—C_{(2)}$	127,6(1)
$C_{(1)}—N_{(2)}—C_{(4)}$	122,0(1)	$S—C_{(6)}—C_{(7)}$	110,9(1)
$S—C_{(1)}—N_{(2)}$	118,9(1)	$N_{(1)}—C_{(1)}—N_{(2)}$	123,7(2)
$O_{(1)}—C_{(2)}—N_{(1)}$	121,8(2)	$O_{(1)}—C_{(2)}—C_{(3)}$	123,4(2)
$N_{(2)}—C_{(4)}—C_{(5)}$	113,0(2)	$O_{(2)}—C_{(4)}—N_{(2)}$	126,0(2)
$O_{(3)}—C_{(7)}—C_{(8)}$	110,3(2)	$O_{(3)}—C_{(7)}—C_{(6)}$	115,6(2)
$C_{(7)}—C_{(8)}—C_{(9)}$	106,5(2)	$C_{(8)}—C_{(9)}—C_{(10)}$	106,9(2)
$O_{(3)}—C_{(10)}—C_{(9)}$	109,2(2)	$O_{(3)}—C_{(10)}—C_{(11)}$	116,1(2)
$O_{(4)}—C_{(11)}—C_{(10)}$	124,4(2)	$O_{(4)}—C_{(11)}—O_{(5)}$	124,6(2)
$O_{(5)}—C_{(12)}—C_{(13)}$	108,0(2)		

TABLE 4. Some Torsion Angles in the I Structure

Atoms	θ°	Atoms	θ°
$C_{(1)}—N_{(1)}—C_{(2)}—O_{(1)}$	1,4(2)	$C_{(1)}—N_{(2)}—C_{(4)}—O_{(2)}$	12,1(3)
$S—C_{(1)}—N_{(1)}—C_{(2)}$	0,9(2)	$S—C_{(1)}—N_{(2)}—C_{(4)}$	179,6(2)
$N_{(1)}—C_{(1)}—N_{(2)}—C_{(4)}$	2,7(3)	$C_{(1)}—S—C_{(6)}—C_{(7)}$	83,2(2)
$N_{(2)}—C_{(1)}—S—C_{(6)}$	11,1(2)	$N_{(1)}—C_{(1)}—S—C_{(6)}$	171,0(3)
$S—C_{(6)}—C_{(7)}—C_{(8)}$	101,3(3)	$C_{(9)}—C_{(10)}—C_{(11)}—O_{(5)}$	4,9(2)
$C_{(10)}—C_{(11)}—O_{(5)}—C_{(12)}$	178,7(3)	$C_{(7)}—C_{(8)}—C_{(9)}—C_{(10)}$	0,6(2)

conformation (or conformations) in which these interactions can be manifested [8]. To study the conformational structure of I-IV by x-ray diffraction analysis we investigated the crystal and molecular structures of I (see Fig. 1 and Tables 2-4).

Two principal planar parts connected by a CH_2—S bridge can be isolated in the I molecule: the furan ring (plane 1) and the amidine fragment $S—C_{(1)}=N_{(1)}N_{(2)}$ (plane 2).

The furan ring is planar within the limits ± 0.003 Å. The ester group is also planar (plane 3; the maximum deviation of the atoms from the mean-square plane does not exceed 0.003 Å) and is turned 4.2° relative to the furan ring.

Let us note some differences in the bond lengths in the furan rings of the I molecule and furan-2-carboxylic acid [9]. Thus the $C_{(2)}—C_{(3)}$, $C_{(2)}—O$, and $C_{(5)}—O$ bonds of the I molecule are significantly longer while the $C_{(3)}—C_{(4)}$ bond is appreciably shorter than the corresponding bonds in the pyromucic acid molecule (1.312, 1.368, 1.287, and 1.446 Å, respectively [9]). The exocyclic $C_{(10)}—C_{(11)}$ bond is longer than the corresponding bond in the furancarboxylic acid molecule (1.414 Å [9]). The ratio of the lengths of the β,β bonds of carbon to the lengths of the α,β bonds serves as one of the criteria of the aromatic character of five-membered heterorings [10]. According to this criterion, the furan ring in the I molecule is more aromatic than in the pyromucic acid molecule.

Two acetyl groupings $O_{(1)}—C_{(2)}—C_{(3)}$ (plane 4) and $O_{(2)}—C_{(4)}—C_{(5)}$ (plane 5) adjoin the amidine fragment [the S, $C_{(1)}$, $N_{(1)}$, and $N_{(2)}$ atoms deviate from plane 2 by 0.003, −0.012, 0.004, and 0.004 Å, respectively]. The angles between planes 2 and 4 and 2 and 5 are 0.8° and 13.0°, respectively. In the six-membered $H_{(1)}—N_{(1)}—C_{(1)}—N_{(2)}—C_{(4)}—O_{(2)}$ ring, which is formed by an $N_{(1)}—H_{(1)}\cdots O_{(2)}$ hydrogen bond and is nonplanar (helical), the $N_{(1)}—H_{(1)}$ and $H_{(1)}\cdots O_{(2)}$ bond lengths and angles $N_{(1)}—H_{(1)}—O_{(2)}$ and $H_{(1)}—O_{(2)}—C_{(4)}$ are 0.855 and 1.963 Å and 125.6° and 96.9°, respectively.

In the CH_2—S grouping, which connects the polar fragments of the molecule, the $C_{(6)}$—S bond length corresponds to the standard length of the C_{sp^3}—S bond (1.817 Å for dialkyl sulfides [11]). The $S—C_{(1)}$ bond is longer than the standard $S—C_{sp^2}$ bond (1.71 Å [12]). The orientation of the substituents relative to the $C_{(6)}$—S bond corresponds to a *gauche* conformation (Fig. 2a), while the $C_{(6)}$—S bond virtually eclipses the $C_{(1)}—N_{(2)}$ multiple bond (Fig. 2b). As a result, the angle between planes 1 and 2 is 96°.

The question arises as to whether other substituents in the furan ring (NO_2, CN, CHO) affect the conformational orientation of the polar fragments in the I-IV molecules and whether, as a result of this effect, contacts that are absent in the I molecule develop between these fragments. To answer this question one may compare the conformations of the I molecule and the 1,4-diacetyl-3-(5-nitrofurfurylthio)-Δ^2-1,2,4-triazoline (V) [13] molecule, which has a structure similar to that of thiourea II. In the nitrofurfuryl V molecule the torsion angles corresponding to angles $C_{(7)}—C_{(6)}—S—C_{(1)}$, $C_{(6)}—S—C_{(1)}—N_{(1)}$, and $C_{(6)}—S—C_{(1)}—N_{(2)}$ are, respectively, 65.0°, 170.6°, and 8.8°, while the

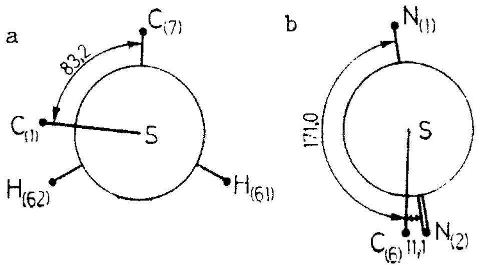

Fig. 2. Newman projection of I along the S—$C_{(6)}$ (a) and S—$C_{(1)}$ (b) bonds.

angle between the planes of the nitrofuran and amidine fragments is 89.9° [13]. The similar geometries of ethoxycarbonylfuran I and nitrofuran V derivatives makes it possible to assume that other substituents will also have just as slight an effect on the conformation of 1,3-diacetyl-2-furfurylthioureas.

Thus x-ray diffraction analysis confirms the PMR spectroscopic data regarding the presence of an intramolecular hydrogen bond (IMHB) in the I-IV molecules and shows that the conformation of these molecules (at least in the crystalline state) excludes filed or dipole-dipole intramolecular interaction between the furan ring and the amidine fragment.

One would think that such factors as the presence of a CH_2—S grouping, which isolates the electronic effects of substituents, the three-dimensional structure of I-IV, and the IMHB in these molecules should exclude the effect of the R substituents on the dynamics of the observed (in the PMR spectra) phenomenon. Nevertheless, the R substituents in the furan ring have a certain "extra-long-range" effect on the dynamic processes in the amidine fragment of I-IV.

EXPERIMENTAL

The PMR spectra of 1 solutions of I-IV in d_6-acetone were recorded with a Jeol 90 Q spectrometer (90 MHz) with tetramethylsilane (TMS) as the internal standard.

The transparent crystals of $C_{13}H_{16}N_2O_5S$ (chloroform—hexane) were triclinic and had the following cell parameters: a = 11.059(3) Å, b = 7.800(2) Å, c = 9.882(3) Å, α = 66.71(2)°, β = 81.72(2)°, γ = 74.55(2)°, V = 754.0(3) Å^3, space group $P\bar{1}$, $Z = 2$. The experimental data were obtained with a PT Syntex automatic diffractometer (Mo K_α emission, β filter, $\theta/2\theta$ scanning up to $2\theta_{max}$ = 48°). We obtained a total of 1910 reflections with $I \geq 3\sigma(I)$. The structure was decoded by the direct method by means of a set of SHELXTL programs [14] with a NOVA 3 computer and was refined within the anisotropic (isotropic for the H atoms) approximation up to divergence factors $R = 0.033$ and $R_w = 0.038$.*

The synthesis and physicochemical characteristics of I-IV were described in [15].

LITERATURE CITED

1. S. Patai (ed.), *The Chemistry of Amidines and Imidates*, J. Wiley, New York (1975), pp. 1-84.
2. V. I. Minkin, L. P. Olekhnovich, and Yu. A. Zhdanov, *The Molecular Design of Tautomeric Systems* [in Russian], Rostovsk. Gosudarstv. Univ., Rostov-on-Don (1977).
3. O. J. Sherer and P. Hornig, *Chem. Ber.*, **101**, 2533 (1967).
4. V. I. Minkin, L. P. Olekhnovich, Yu. A. Zhdanov, I. E. Mikhailov, V. P. Metlushenko, N. M. Ivanchenko, and N. I. Borisenko, *Zh. Org. Khim.*, **12**, 1261 (1976).
5. V. V. Negrebetskii, A. D. Sinitsa, V. I. Kal'chenko, L. I. Atamas', and L. N. Markovskii, *Zh. Obshch. Khim.*, **53**, 343 (1983).
6. M. I. Kabachnik, *Zh. Vsesoyuzn. Khim. Obshchestva*, **7**, 263 (1962).
7. G. D. Krapivin, E. B. Usova, and V. G. Kul'nevich, *The Chemistry and Technology of Furan Compounds*, V. G. Kul'nevich (ed.), Krasnodarsk. Politekhn. Inst., Krasnodar (1987), p. 44.
8. F. Becker, *Z. Naturf.*, **16b**, 236 (1961).
9. P. Hudson, *Acta Cryst.*, **15**, 919 (1962).

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*The anisotropic temperature factors of the nonhydrogen atoms can be obtained from the authors.

10. A. F. Pozharskii, *Theoretical Foundations of the Chemistry of Heterocycles* [in Russian], Khimiya, Moscow (1985).
11. A. Gordon and R. Ford, *The Chemist's Guide* [Russian translation], Mir, Moscow (1976), p. 129.
12. R. Gillespie, *Molecular Geometry* [Russian translation], Mir, Moscow (1975), pp. 31, 32.
13. E. B. Usova, G. D. Krapivin, V. E. Zavodnik, and V. G. Kul'nevich, *Khim. Geterotsikl. Soedin.*, No. 7, 931 (1990).
14. G. M. Sheldrick, *Computational Crystallography*, Oxford University Press, New York—London (1982), p. 506.
15. E. B. Usova, G. D. Krapivin, and V. G. Kul'nevich, *Khim. Geterotsikl. Soedin.*, No. 4, 557 (1990).

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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