S-ALKYLTHIOSEMICARBAZONIUM SALTS IN THE SYNTHESIS OF 1,2,4-TRIAZOLINES. MOLECULAR STRUCTURE OF 1,4-DIACETYL-3-(5-NITROFURFURYLTHIO)-5-(2-FURYL)-Δ²-1,2,4-TRIAZOLINE

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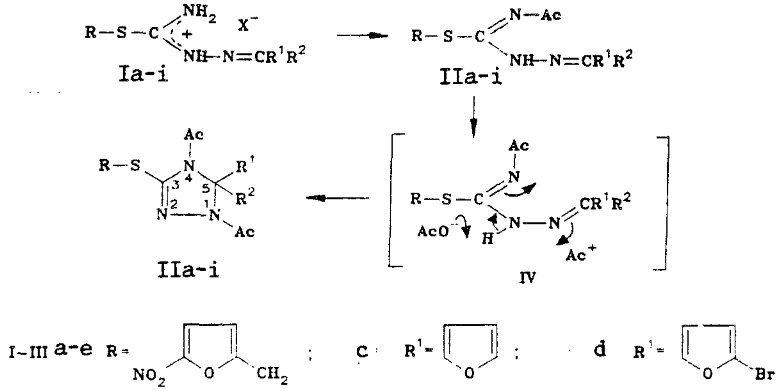
UDC 547.792'497.1:548.737

Acylation of S-alkylthiosemicarbazonium salts with acetic anhydride leads to the formation of 1,4-diacetyl-Δ²-1,2,4-triazolines. It was also demonstrated, based on x-ray structural analysis, that the triazoline ring in the molecular structure of 1,4-diacetyl-3-(5-nitrofurfurylthio)-5-(2-furyl)-Δ²-1,2,4-triazoline exists in an envelope or bent conformation.

The acylation of monoacylhydrazones represents a general method for the synthesis of 4-acyl-1,3,4-oxadiazolines [1-3]. It was of interest to us to apply this reaction to the synthesis of triazolines, using nitrogen analogs of acylhydrazones as the starting materials. We have prepared this type of compound by the acylation of S-alkylthiosemicarbazonium salts [4].

By studying the acylation of salts I with acetic anhydride we have found conditions which are suitable for the preparation of triazoline derivatives III in high yields (Table 1). In some cases the intermediate monoacyl derivatives II could also be isolated, and they were converted upon heating in acetic anhydride to the corresponding triazolines III.



f. $R=CH_3$, g–i $R=C_6H_5CH_2$; a $R^1=C_6H_5$, b $R^1=C_6H_4OCH_3$-4; e $R^1=CH_\alpha=CH_3C_6H_5$, f $R^1=C_6H_4Cl$-o, g $R^1=C_6H_3Cl_2$-2,4, h $R^1=CH_3$, i $R^1=R^2=(CH_2)_6$; a–g $R^2=H$, h $R^2=$ $=CH_3$; a–e $X=Br$, f $X=I$, g–i $X=Cl$

It is known that compounds similar to salts I are susceptible to ring-chain tautomerism (see, for example, [5-7]). However, judging from the PMR spectra of compounds Ia-g ($R^2 = H$), which contain only one set of signals involving the CH=N proton in the 8.2-8.5 ppm region (Table 1), we conclude that salts I exist as acyclic structures. The monoacyl derivatives II also exist in the acyclic structure.

In contrast, in the PMR spectra of triazolines IIIa-g the signal in the 8.2-8.5 ppm region is missing, and there is instead a signal for the 5-H proton in the triazoline ring in the region 6.8-7.2 ppm.

The IR spectra of salts I contain three bands due to NH stretching vibrations in the 3150-3320 cm^{-1} region, as well as an intense overtone band at 1640-1660 cm^{-1} (Table 1). The spectra of their monoacyl derivatives II exhibit only one narrow NH band (at 3300-3320 cm^{-1}), and an intense CO absorption band (at 1695-1720 cm^{-1}). The spectra of triazolines III are characterized by the absence of absorption bands in the 3150-3400 cm^{-1} region, and by the presence of two highly intense bands at 1635-1673 and 1690-1720 cm^{-1}, attributable to amide carbonyl group stretching vibrations.

Krasnodar Polytechnical Institute, Krasnodar 350670. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 931-937, July, 1990. Original article submitted July 27, 1988; revision submitted May 12, 1989.

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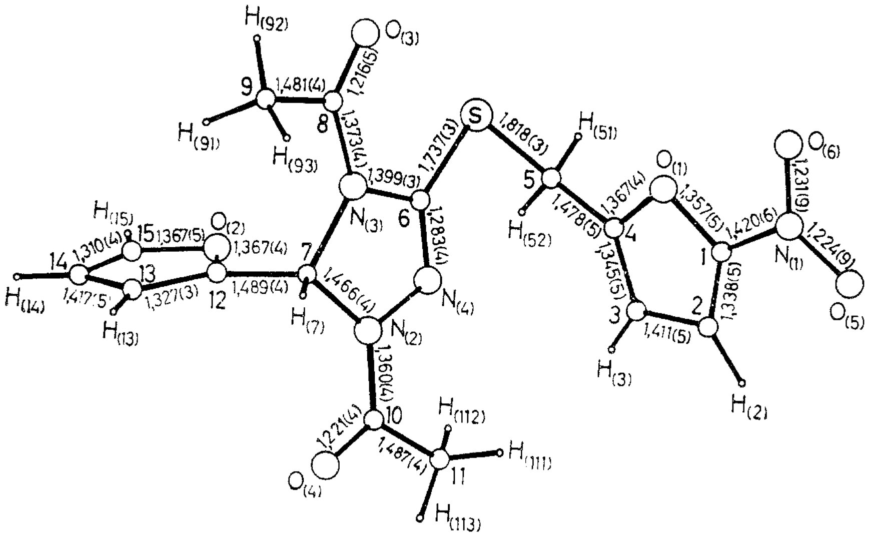

Fig. 1. Projection of a three-dimensional model of the molecular structure of compound IIIc.

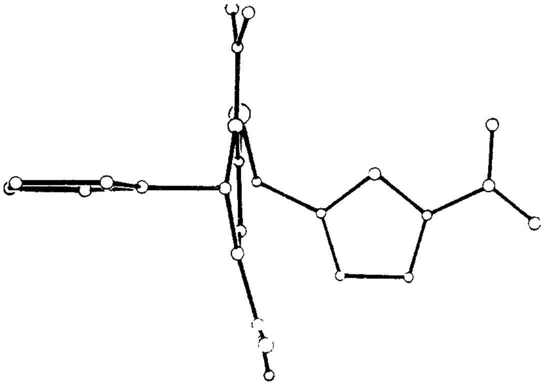

Fig. 2. Three-dimensional model projection of the molecular structure of compound IIIc on the plane of the nitrofuran ring.

Since there is no information herein concerning the geometry of the triazoline ring in these compounds, we carried out an x-ray structural investigation of compound IIIc.

The value of the $C_{(6)}$–$N_{(1)}$ interatomic distance 1.238(4) Å is indicative of a Δ^2-position for the multiple bond in the triazoline ring. All the other interatomic distances are normal and in excellent accord with literature data [8]. Thus, the $C_{(6)}$–$N_{(3)}$ bond length is shorter than the bond lengths for the other C–N single bonds, but comparable to the bond lengths for the $C_{(8)}$–$N_{(3)}$ and $C_{(10)}$–$N_{(2)}$ amide bonds, since formation of the first bond involves a carbon atom in its sp^2-hybridized state. This same factor is responsible for the differences in the $C_{(6)}$–S and $C_{(5)}$–S interatomic distances.

The triazoline ring exists in a bent or envelope conformation; the $N_{(2)}$, $N_{(3)}$, $N_{(4)}$, and $C_{(6)}$ atoms lie in one plane (plane 1, with a maximum deviation from the root-mean-square plane of less than 0.002 Å) (Fig. 1). Atom $C_{(7)}$ deviates from plane 1 by 0.16 Å, while the angle between the two planes in the envelope is 6.9°. The $O_{(3)}$, $C_{(8)}$, $C_{(9)}$ and $O_{(4)}$, $C_{(10)}$, $C_{(11)}$ acetyl groups are bent away from plane 1 by 8.9 and 14.2°, respectively, in opposite directions.

The $O_{(2)}$–$C_{(12)}$...$C_{(15)}$ furan ring is planar within 0.003 Å limits and is oriented rigidly perpendicular to plane 1, such that the $C_{(12)}$–$C_{(13)}$, multiple bond is screened or shielded by the $C_{(7)}$–$H_{(7)}$ single bond. The bond lengths and bond angles within the furan ring correspond to their standard values (see Tables 2-4).

The $O_{(1)}$–$C_{(2)}$...$C_{(4)}$ furan ring is also planar within 0.003 Å and exhibits standard bond lengths for a nitrofuran derivative. The nitrogen atom in the nitro group is oriented within the plane of the furan ring, while at the same time the carbon

TABLE 1. Characteristics of Newly Synthesized Compounds

Compound	Molecular formula *	mp, °C	IR spectrum, cm^{-1}	PMR spectrum, δ, ppm, J, Hz				Yield, %
				R	R¹	R²	Ac (NH)	
Ia	$C_{13}H_{13}BrN_4O_3S$	165	1650, 3180, 3200, 3300	4,32 (s, 2H, CH_2S); 6,35 (d, 1H, 3-H); 6,93 (d, 1H, 4-H); $J_{34}=4,0$	7,07 ... 7,47 (m, 5H, C_6H_5)	8,10	—	80
Ib	$C_{14}H_{15}BrN_4O_4S$	160	1650, 3180, 3230, 3300	4,32 (s, 2H, CH_2S); 6,36 (d, 1H, 3-H); 6,96 (d, 1H, 4-H); $J_{34}=4,0$	3,50 (s, 3H, OCH_3); 6,60 (d, 2H, m-H); 7,34 (d, 2H, o-H); $J_{om}=9,0$	8,22	—	88
Ic	$C_{11}H_{11}BrN_4O_4S$	170	1650, 3160, 3230, 3300	4,32 (s, 2H, CH_2S); 6,50 (d, 1H, 3-H); 6,93 (d, 1H, 4-H); $J_{34}=4,0$	6,13 (dd, 1H, 4-H); 6,66 (dd, 1H, 3-H); 7,21 (dd, 1H, 5-H); $J_{34}=3,6$; $J_{35}=0,6$; $J_{45}=1,7$	7,92	—	80
Id	$C_{11}H_{10}Br_2N_4O_4S$	160	1650, 3150, 3230, 3300	4,33 (s, 2H, CH_2S); 6,37 (d, 1H, 3-H); 6,98 (d, 1H, 4-H); $J_{34}=4,0$	6,08 (d, 1H, 4-H); 6,66 (d, 1H, 3-H); $J_{34}=4,0$	7,83	—	72
Ie	$C_{15}H_{15}BrN_4O_3S$	175	1640, 3180, 3210, 3280	4,40 (s, 2H, CH_2S); 6,94 (d, 1H, 3-H); 7,62 (d, 1H, 4-H); $J_{34}=4,0$	7,03 (dd, 1H, α-H); 7,20 (d, 1H, β-H); 7,0 ... 7,7 (m, 5H, C_6H_5); $J_{\alpha\beta}=16,0$; $J_{\alpha x}=8,0$	8,27 (d, 1H) $J_{\alpha x}=8,0$	—	50
If	$C_9H_{11}ClN_3S$	185 ... 187	1610, 3100, 3190, 3220	—	—	—	—	57
Ig	$C_{15}H_{14}Cl_3N_3S$	253 ... 255	1640, 3220, 3280	4,10 (s, 2H, CH_2S); 6,97 (s, 5H, C_6H_5)	6,57 ... 7,55 (m, 3H, $C_6H_3Cl_2$)	8,25	—	80
Ih	$C_{11}H_{16}ClN_3S$	193 ... 195	1640, 3100, 3200, 3280	4,07 (s, 2H, CH_2S); 7,0 (s, 5H, C_6H_5)	1,69 (s, 6H, $(CH_3)_2C$)	—	—	95
Ii	$C_{15}H_{22}ClN_3S$	173 ... 175	1640, 3180, 3280	4,07 (s, 2H, CH_2S); 7,0 (s, 5H, C_6H_5)	1,25 (br.s, 12H, $(CH_2)_6$)	—	—	78
IIa	$C_{15}H_{14}N_4O_4S$	112 ... 113	1713, 3330	4,20 (s, 2H, CH_2S); 6,45 (d, 1H, 3-H); 7,20 (d, 1H, 4-H); $J_{34}=3,7$	7,1 ... 7,1 (m, 5H, C_6H_5)	8,33	2,23 (9,36)	60
IIb	$C_{16}H_{16}N_4O_5S$	161 ... 162	1730, 3330	4,23 (s, 2H, CH_2S); 6,45 (d, 1H, 3-H); 7,22 (d, 1H, 4-H); $J_{34}=3,7$	3,82 (s, 3H, OCH_3); 7,0 ... 7,3 (m, 4H, C_6H_4)	8,25	2,25 (9,38)	49
IIc	$C_{13}H_{12}N_4O_5S$	114 ... 115	1703, 3300	4,18 (s, 2H, CH_2S); 6,45 (d, 1H, 3-H); 7,13 (d, 1H, 4-H); $J_{34}=3,6$	6,47 (dd, 1H, 4-H); 6,80 (dd, 1H, 3-H); 7,48 (dd, 1H, 5-H); $J_{34}=3,6$; $J_{45}=1,7$; $J_{35}=0,6$	8,15	2,10 (9,70)	49

IId	$C_{13}H_{11}BrN_4O_5S$	118...119	1724, 3335	4,23 (s, 2H, CH_2S); 6,44 (d, 1H, 3-H); 7,13 (d, 1H, 4-H); $J_{34}=4,0$	6,36 (d, 1H, 4-H); 6,75 (d, 1H, 3-H); $J_{34}=3,6$	8,02	2,11 (9,60)	84
IIIa	$C_{17}H_{16}HN_4O_5S$	164...165	1665, 1695	4,25 (s, 2H, CH_2S); 6,53 (d, 1H, 3-H); 7,18 (d, 1H, 4-H); $J_{34}=3,7$	7,0...7,5 (m, 5H, C_6H_5)	7,00	2,20; 2,03	69 (60)**
IIIb	$C_{18}H_{18}N_4O_6S$	132...133	1673, 1703	4,25 (s, 2H, CH_2S); 6,51 (d, 1H, 3-H); 7,15 (d, 1H, 4-H); $J_{34}=4,0$	3,72 (s, 3H, OCH_3); 6,75 (d, 2H, *o*-H); 7,25 (d, 2H, m-H); $J_{oм}=9,0$	6,85	1,85; 2,10	63
IIIc	$C_{15}H_{14}N_4O_6S$	150...152	1665, 1697	4,25 (s, 2H, CH_2S); 6,50 (d, 1H, 3-H); 7,20 (d, 1H, 4-H); $J_{34}=3,7$	6,35 (dd, 1H, 4-H); 6,53 (dd, 1H, 3-H); 7,35 (dd, 1H, 5-H); $J_{34}=3,5$: $J_{45}=1,92$; $J_{35}=1,05$	7,00	2,03; 2,20	80 (52)**
IIId	$C_{15}H_{13}BrN_4O_6S$	144...145	1665, 1695	4,25 (s, 2H, CH_2S); 6,45 (d, 1H, 3-H); 7,15 (d, 1,H, 4-H); $J_{34}=3,7$	6,25 (d, 1H, 3-H); 6,52 (d, 1H, 4-H); $J_{34}=3,6$	6,93	2,05; 2,17	69
IIIe	$C_{19}H_{18}N_4O_5S$	105	1665, 1696	4,35 (s, 2H, CH_2S); 6,68 (d, 1,H, 3-H); 7,20 (d, 1H, 4-H); $J_{34}=3,7$	6,22 (dd, 1H, α-H); 7,10 (d, 1H, β-H); $J_{\alpha\beta}=16,0$; $J_{\alpha5}=7,5$; 7,1...7,7 (m, 5H, C_6H_5)	6,70 (d, 1H)	2,06; 2,16	50
IIIf	$C_{13}H_{14}ClN_3O_2S$	133...134	1635, 1696	2,42 (s, 3H, SCH_3)	7,35 (s, 4H, C_6H_4Cl)	6,90	1,92; 2,10	45
IIIg	$C_{19}H_{17}Cl_2N_3O_2S$	140...142	1665, 1690	4,23 (s, 2H, CH_2S); 7,30 (s, 5H, C_6H_5)	7,15...7,65 (m, 3H, $C_6H_3Cl_2$)	7,20	1,93; 2,06	42
IIIh	$C_{15}H_{19}N_3O_2S$	111...113	1660, 1680	4,13 (s, 2H, CH_2S); 7,25 (s, 5H, C_6H_5)	1,90 (s, 6H, $C(CH_3)_2$)		2,13; 2,23	59
IIIi	$C_{19}H_{25}N_3O_2S$	135...137	1660, 1690	4,20 (s, 2H, CH_2S); 7,28 (s, 5H, C_6H_5)	1,68 (m, 12H, $(CH_2)_2$)		2,18; 2,30	56

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*The composition of compounds I, IIIe-i was confirmed by the results of C, H, and N elemental analysis; compounds II and IIIa-d by C, H, and S analysis.

**Using method B.

TABLE 2. Atomic Coordinates (×10^4, for H atoms ×10^3) in the Molecular Structure of IIIc

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
S	8437(2)	629(1)	788(1)	$C_{(10)}$	3703(3)	2444(2)	3580(2)
$O_{(1)}$	9693(4)	−1220(3)	2508(3)	$C_{(11)}$	2975(4)	1187(3)	3347(3)
$O_{(2)}$	3837(6)	3892(4)	995(3)	$C_{(12)}$	4558(3)	4456(2)	2260(2)
$O_{(3)}$	9859(6)	2964(4)	1484(4)	$C_{(13)}$	3977(4)	5682(3)	2598(3)
$O_{(4)}$	3922(5)	3425(4)	4372(3)	$C_{(14)}$	2814(5)	5228(3)	1489(4)
$O_{(5)}$	11283(8)	−2153(6)	5241(4)	$C_{(15)}$	2769(5)	4844(3)	573(3)
$O_{(6)}$	12763(7)	−1387(4)	4217(5)	$H_{(2)}$	746(4)	−226(3)	404(3)
$N_{(1)}$	11340(8)	−1721(5)	4382(5)	$H_{(3)}$	544(4)	−165(3)	211(2)
$N_{(2)}$	4894(3)	2466(2)	2836(2)	$H_{(51)}$	816(3)	−146(2)	4(2)
$N_{(3)}$	7380(3)	2970(2)	2315(2)	$H_{(52)}$	621(3)	−84(2)	26(2)
$N_{(4)}$	5224(3)	1351(2)	2037(2)	$H_{(7)}$	621(3)	410(2)	384(6)
$C_{(1)}$	9619(5)	−1634(3)	3502(3)	$H_{(91)}$	816(4)	542(2)	286(2)
$C_{(2)}$	7888(5)	−1904(3)	3471(3)	$H_{(92)}$	1015(4)	513(3)	298(3)
$C_{(3)}$	6761(4)	−1630(3)	2373(3)	$H_{(93)}$	928(4)	490(3)	389(3)
$C_{(4)}$	7188(4)	−1229(3)	1819(3)	$H_{(111)}$	392(3)	62(2)	379(2)
$C_{(5)}$	7539(4)	−872(3)	626(3)	$H_{(112)}$	280(3)	63(2)	247(2)
$C_{(6)}$	7035(3)	1680(2)	1759(2)	$H_{(113)}$	174(3)	133(2)	359(2)
$C_{(7)}$	5799(4)	3603(3)	2952(2)	$H_{(13)}$	430(4)	627(2)	345(2)
$C_{(8)}$	8857(4)	3544(3)	2224(3)	$H_{(14)}$	229(3)	674(2)	142(2)
$C_{(9)}$	9166(5)	4862(3)	3067(4)	$H_{(15)}$	229(3)	459(3)	−26(3)

TABLE 3. Selected Bond Angle Values in the Molecular Structure of IIIc

Atoms	Angle, deg	Atoms	Angle, deg
$C_{(5)}$—S—$C_{(6)}$	99,9(2)	$O_{(1)}$—$C_{(4)}$—$C_{(5)}$	106,3(3)
$C_{(1)}$—$O_{(1)}$—$C_{(4)}$	104,7(3)	$C_{(4)}$—$C_{(5)}$—S	115,1(2)
$C_{(12)}$—$O_{(2)}$—$C_{(15)}$	104,9(3)	S—$C_{(6)}$—$N_{(4)}$	123,7(2)
$O_{(5)}$—$N_{(1)}$—$O_{(6)}$	125,1(5)	$N_{(3)}$—$C_{(6)}$—$N_{(4)}$	114,4(2)
$O_{(5)}$—$N_{(1)}$—$C_{(1)}$	116,2(6)	$N_{(2)}$—$C_{(7)}$—$C_{(12)}$	112,7(2)
$N_{(4)}$—$N_{(2)}$—$C_{(7)}$	113,0(2)	$N_{(3)}$—$C_{(7)}$—$C_{(12)}$	111,7(2)
$N_{(4)}$—$N_{(2)}$—$C_{(10)}$	122,4(2)	$O_{(3)}$—$C_{(8)}$—$N_{(3)}$	119,9(3)
$C_{(6)}$—$N_{(3)}$—$C_{(7)}$	107,3(2)	$O_{(3)}$—$C_{(8)}$—$C_{(9)}$	122,8(3)
$C_{(6)}$—$N_{(3)}$—$C_{(8)}$	125,8(2)	$O_{(4)}$—$C_{(10)}$—$C_{(11)}$	124,4(3)
$N_{(2)}$—$N_{(4)}$—$C_{(6)}$	105,6(2)	$N_{(2)}$—$C_{(10)}$—$C_{(11)}$	115,8(2)
$O_{(1)}$—$C_{(1)}$—$N_{(1)}$	116,5(4)	$O_{(2)}$—$C_{(12)}$—$C_{(7)}$	115,6(2)
$N_{(1)}$—$C_{(1)}$—$C_{(2)}$	130,8(4)	$O_{(2)}$—$C_{(12)}$—$C_{(13)}$	110,4(3)
$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	107,5(3)	$C_{(12)}$—$C_{(13)}$—$C_{(14)}$	106,7(2)
$C_{(1)}$—$C_{(2)}$—$C_{(3)}$	104,8(3)	$C_{(13)}$—$C_{(14)}$—$C_{(15)}$	106,3(3)
$O_{(1)}$—$C_{(4)}$—$C_{(3)}$	110,3(3)	$C_{(14)}$—$C_{(15)}$—$O_{(2)}$	111,6(3)

TABLE 4. Selected Torsional Angle Values in the Molecular Structure of IIIc

Atoms	Angle, deg	Atoms	Angle, deg
$C_{(6)}$—S—$C_{(5)}$—$C_{(4)}$	65,9(3)	$C_{(7)}$—$N_{(2)}$—$C_{(10)}$—$C_{(11)}$	178,1(4)
$C_{(5)}$—S—$C_{(6)}$—$N_{(3)}$	170,6(2)	$N_{(1)}$—$N_{(2)}$—$C_{(10)}$—$C_{(11)}$	9,4(3)
$C_{(5)}$—S—$C_{(6)}$—$N_{(4)}$	8,8(3)	$C_{(7)}$—$N_{(3)}$—$C_{(6)}$—$N_{(1)}$	6,9(3)
$C_{(4)}$—$O_{(1)}$—$C_{(1)}$—$N_{(1)}$	179,8(2)	$C_{(6)}$—$N_{(3)}$—$C_{(7)}$—$N_{(2)}$	9,6(3)
$C_{(15)}$—$O_{(2)}$—$C_{(12)}$—$C_{(7)}$	179,9(3)	$C_{(8)}$—$N_{(3)}$—$C_{(7)}$—$N_{(2)}$	173,6(2)
$O_{(5)}$—$N_{(1)}$—$C_{(1)}$—$O_{(1)}$	176,6(4)	$C_{(7)}$—$N_{(3)}$—$C_{(8)}$—$C_{(9)}$	14,5(2)
$C_{(7)}$—$N_{(2)}$—$N_{(4)}$—$C_{(6)}$	6,7(3)	$C_{(7)}$—$C_{(12)}$—$C_{(13)}$—$C_{(14)}$	179,5(3)

atom for the $C_{(5)}$ methylene unit deviates from the plane by 0.07 Å. The nitro group is rotated along the $C_{(1)}$–$N_{(1)}$ bond by 2.6° relative to the furan ring.

The best picture illustrating the mutual orientation of heterocycles and substituents is given by a projection of the molecular model structure on the plane of the nitrofuran ring (Fig. 2). We note that the angle between plane 1 and that of the nitrofuran ring is equal to 89.5°.

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrophotometer using suspensions in Vaseline oil. PMR spectra were obtained on a Tesla BS-467A (60 MHz) spectrometer using solutions in CF_3COOD (compounds I) and $CDCl_3$ (compounds II and III) versus HMDS as internal standard. The course of reactions and the purity of the resulting products were monitored by TLC using Silufol-254 plates and toluene–ethanol, 20:3, as the eluting system.

Transparent crystals of composition $C_{15}H_{14}N_4O_6S$ for compound IIIc (from chloroform–hexane, 1:1) are triclinic: a = 7.355(2), b = 11.098(2), c = 11.292(2) Å, α = 108.69(1), β = 104.01(1), and γ = 81.94(1)°, V = 845.2(3) Å^3. Space group P1, Z = 2. The experimental data were collected on a PT Syntex automated diffractometer using Mo Kα irradiation with a β-filter and $\theta/2\theta$-scanning in the range $2\theta_{max}$ = 50°. A total of 2032 reflections with $I \geq 3\sigma(I)$ was obtained. The structure was solved by direct methods using the SHELXTL [9] system of programs on a NOVA 3 computer, and was refined with anisotropic (isotropic in the case of H atoms) approximations to give a final discrepancy factor R = 0.04 and R_w = 0.043.*

3-(5-Nitrofurfuryl)-1-(furfurylidene-2)thiosemicarbazonium Bromide (Ic). To a hot solution of 8.5 g (50 mmoles) furfural thiosemicarbazone in 50 ml ethanol was added 10.3 g (50 mmoles) 5-nitrofurfuryl bromide. The mixture was refluxed for 10-20 min, cooled, and diluted with 100 ml ether. The resulting precipitate was separated and washed with ether. Compounds Ia, b, d, e, g-i were prepared analogously.

3-Methyl-1-(4-chlorobenzylidene)thiosemicarbazonium Iodide (If). To a solution of 3.18 g (15 mmoles) 4-chlorobenzaldehyde thiosemicarbazone in 50 ml alcohol was added 2.2 g (15 mmoles) methyl iodide, and the solution was refluxed for 1 h. The solvent was evaporated to one half its original volume, 50 ml ether was added, and the resulting precipitate was removed by filtration.

4-Acetyl-3-(5-nitrofurfuryl)-1-(furfurylidene-2)thiosemicarbazide (IIc). A mixture of 2.0 g (55 mmoles) compound Ic, 0.45 g (55 mmoles) sodium acetate, 30 ml acetic anhydride, and 15 ml water was stirred at room temperature for 30-40 min until it was completely homogeneous (the temperature of the reaction mixture increases exothermically to 40-60°C). After addition of 50 ml water and cooling an oil was deposited, which was crystallized in the cold.

Compounds IIa, b, d were prepared analogously.

1,4-Diacetyl-3-(5-nitrofurfurylthio)-5-(2-furyl)-Δ^2-1,2,4-triazine (IIIc). A. A mixture of 7.6 g (20 mmoles) salt Ic and 1.64 g (20 mmoles) sodium acetate in 100 ml acetic anhydride was stirred for 1 h at 100°C. The mixture was cooled and 100 ml of 10% NaOH solution was added, maintaining the temperature between 50-60°C. The resulting solution was cooled to 0°C and the precipitate which deposited was recrystallized from chloroform.

Compounds IIIa, b, d-i were prepared in an analogous manner.

B. A solution of 1.7 g (5 mmoles) compound IIc in 20 ml acetic anhydride was boiled for 1 h. The product was isolated and purified as described above.

Compound IIIa was obtained in an analogous manner.

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*Values of the anisotropic thermal parameters can be obtained from the authors.