Russian Journal of Organic Chemistry, Vol. 37, No. 5, 2001, pp. 721–723. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 5, 2001, pp. 759–761.
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Crystalline and Molecular Structure of 2-Amino-5-phenyl-1,3,4-thiadiazole

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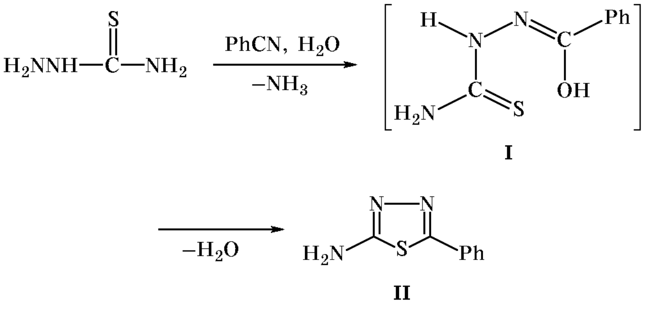
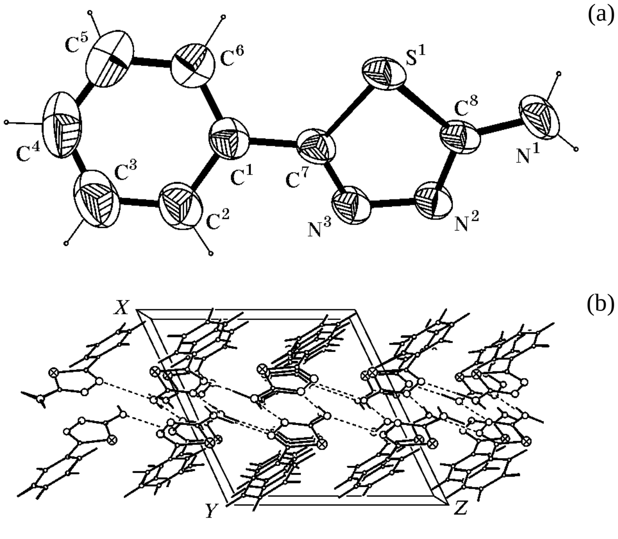
Received February 28, 2000

Abstract—The crystalline and molecular structure of 2-amino-5-phenyl-1,3,4-thiadiazole was studied by the X-ray diffraction method. $C_8H_7N_3S$. Monoclinic crystals: $a = 11.085(3)$, $b = 7.544(3)$, $c = 11.180(3)$ Å; $\beta = 115.22(2)°$; $V = 845.8(5)$ Å^3; $d_{calc} = 1.404$ g/cm^3; $\mu(\mathrm{Mo}K_\alpha) = 0.325$ mm^{-1}; $Z = 4$; space group $P2_1/c$. Molecules of 2-amino-5-phenyl-1,3,4-thiadiazole in crystal form dimers through intermolecular hydrogen bonds, which are arranged in infinite layers parallel to the *xy* plane.

Interest in 1,3,4-thiadiazole derivatives is explained by wide spectrum of their biological, pharmacological, and antileukemic activity [1–3]. Some compounds of this series were synthesized and were examined mainly by ^{1}H NMR and IR spectroscopy [4]. The present communication reports on the results of X-ray analysis of a single crystal of 2-amino-5-phenyl-1,3,4-thiadiazole (**II**), which was synthesized by reaction of thiosemicarbazide with benzonitrile [5]. Initially, hydrolysis of benzonitrile in trifluoroactic acid occurs, and the hydrolysis product reacts with thiosemicarbazide to give intermediate **I** which undergoes intramolecular cyclization to 2-amino-5-phenyl-1,3,4-thiadiazole (**II**).



The IR spectrum of compound **II** contains bands typical of C=N bond vibrations at 1630 (ν_s) and 1508 cm^{-1} (ν_{as}); stretching vibrations of the =N−N=, N=C−N, and C−S fragments give rise to absorption at 1060, 1556, and 912 cm^{-1}, respectively [6]. In the ^{1}H NMR spectrum of **II** a triplet and two doublet signals from protons of the phenyl ring were present at δ δ 7.38, 7.66, and 7.73 ppm. The NH$_2$ signal was partially overlapped by the aromatic triplet. Figure shows the structure of molecule **II** and projection of the crystal lattice on the *xz* plane. Table 1 contains coordinates of non-hydrogen atoms and their equivalent isotropic temperature factors; the bond lengths and angles are collected in Table 2; Table 3 gives deviations of atoms from the mean-square planes, and Table 4 contains parameters of hydrogen bonds.



(a) Molecular and (b) crystalline structure of 2-amino-5-phenyl-1,3,4-thiadiazole (**II**).

1070-4280/01/3705-0721$25.00

Table 1. Coordinates of non-hydrogen atoms ($\times 10^4$) and their equivalent isotropic temperature factors ($\times 10^3$, Å^2) in the molecule of 2-amino-5-phenyl-1,3,4-thiadiazole (**II**)

Atom	*x*	*y*	*z*	U^a
S^1	6819 (1)	–978 (1)	–532 (1)	49 (1)
C^1	7709 (3)	1182 (4)	1739 (3)	46 (1)
C^2	8424 (4)	1130 (5)	3102 (4)	64 (1)
C^3	9164 (5)	2568 (7)	3768 (5)	82 (1)
C^4	9202 (4)	4067 (6)	3093 (5)	82 (1)
C^5	8495 (5)	4161 (5)	1757 (5)	81 (1)
C^6	7742 (4)	2714 (5)	1068 (4)	64 (1)
C^7	6963 (3)	–386 (4)	1028 (3)	42 (1)
C^8	5919 (3)	–2802 (4)	–427 (3)	44 (1)
N^1	5409 (4)	–3989 (4)	–1405 (3)	70 (1)
N^2	5762 (3)	–2886 (3)	664 (2)	51 (1)
N^3	6381 (3)	–1488 (3)	1502 (2)	49 (1)

[a] $U = (\Sigma \Sigma U_{ij} a_i^* a_j^* a_i a_j)/3$.

Table 2. Bond lengths and bond angles in the molecule of 2-amino-5-phenyl-1,3,4-thiadiazole (**II**)

Bond	*d*, Å	Bond	*d*, Å
$S^1{-}C^8$	1.732 (3)	$C^4{-}H^4$	0.91 (4)
$S^1{-}C^7$	1.741 (3)	$C^5{-}C^6$	1.391 (5)
$C^1{-}C^6$	1.386 (4)	$C^5{-}H^5$	0.89 (4)
$C^1{-}C^2$	1.389 (5)	$C^6{-}H^6$	0.96 (4)
$C^1{-}C^7$	1.467 (4)	$C^7{-}N^3$	1.296 (3)
$C^2{-}C^3$	1.373 (5)	$N^3{-}N^2$	1.383 (3)
$C^2{-}H^2$	0.94 (4)	$N^2{-}C^8$	1.306 (3)
$C^3{-}C^4$	1.369 (6)	$C^8{-}N^1$	1.338 (4)
$C^3{-}H^3$	0.89 (5)	$N^1{-}H^1$	0.899 (17)
$C^4{-}C^5$	1.363 (6)	$N^1{-}H^2$	0.886 (19)
Angle	**ω, deg**	**Angle**	**ω, deg**
$C^8S^1C^7$	86.88 (13)	$C^6C^5H^5$	117 (3)
$C^6C^1C^2$	118.9 (3)	$C^1C^6C^5$	120.0 (4)
$C^6C^1C^7$	121.0 (3)	$C^1C^6H^6$	122 (2)
$C^2C^1C^7$	120.0 (3)	$C^5C^6H^6$	117 (2)
$C^3C^2C^1$	120.4 (4)	$N^3C^7C^1$	124.0 (3)
$C^3C^2H^2$	127 (2)	$N^3C^7S^1$	113.3 (2)
$C^1C^2H^2$	112 (2)	$C^1C^7S^1$	122.6 (2)
$C^4C^3C^2$	120.2 (4)	$C^7N^3N^2$	113.7 (2)
$C^4C^3H^3$	122 (3)	$C^8N^2N^3$	111.8 (2)
$C^2C^3H^3$	118 (3)	$N^2C^8N^1$	123.6 (3)
$C^5C^4C^3$	120.6 (4)	$N^2C^8S^1$	114.3 (2)
$C^5C^4H^4$	121 (2)	$N^1C^8S^1$	122.1 (2)
$C^3C^4H^4$	118 (2)	$C^8N^1H^1$	119.5 (17)
$C^4C^5C^6$	119.9 (4)	$C^8N^1H^2$	122 (3)
$C^4C^5H^5$	123 (3)	$H^1N^1H^2$	118 (3)

Unshared electron pairs on the N^1 and S atoms in molecule **II** are conjugated with the C=N double bonds. This follows from the lengths of the $N^2{-}C^8$, $N^3{-}C^7$, $N^2{-}N^3$ bonds: 1.306 (3), 1.296 (3), and 1.383 (3) Å, respectively (Table 2). The endocyclic N=C bond lengths are similar; they occupy an intermediate place between standard values for double and single carbon–nitrogen bonds. The N^1 atom deviates from the mean-square plane of the heteroring by only 0.0024 Å (Table 3), indicating the existence of conjugation between the unshared electron pair on the amino nitrogen atom and the heterocycle; this means that the exocyclic amino group is coplanar to the thiadiazole ring. The dihedral angle between the latter and the benzene ring is 34.6°. The C–C bonds in the benzene ring have approximately equal lengths in the range 1.363–1.391 Å. The $C^1{-}C^7$ bond which links the benzene and thiadiazole rings is appreciably extended [to 1.467 (4) Å]. This may be due to specific features of the crystal packing where cyclic fragments of molecule **II** are arranged at a certain angle to each other. As a result, only a weak interaction between their π-electron systems is possible.

The crystalline structure of thiadiazole **II** is characterized by the presence of two independent molecules **A** and **B** in a unit cell; they form a pseudocentrosymmetric dimer through symmetric hydrogen bonds like $N^{1a}{-}H\cdots N^{2b}$ and $N^{1b}{-}H\cdots N^{2a}$. The dimers in crystal are linked through intermolecular $N{-}H\cdots N$ hydrogen bonds involving proton of the amino group and that nitrogen atom of the thiadiazole ring which does not participate in the dimer formation (Table 4). Molecules of type **A** (or **B**) suffer symmetry transformations with respect to the sliding reflection plane and are linked through intermolecular hydrogen bonds, forming infinite bilayers which are parallel to the *xy* plane. Each monolayer of a given bilayer consists of molecules of a single type (**A** or **B**).

EXPERIMENTAL

The IR spectra (400–4000 cm^{-1}) were recorded in KBr on a Specord 75IR spectrometer. The ^{1}H NMR spectra were obtained on XL-100 and XL-200 instruments using CD_3OD as solvent and HMDS as internal reference.

2-Amino-5-phenyl-1,3,4-thiadiazole (II) [5]. Trifluoroacetic acid, 150 ml, was added to a mixture of 50 g (0.55 mol) of thiosemicarbazide and 51.5 g (0.5 mol) of benzonitrile. The mixture was refluxed for 6 h under stirring and cooled to room temperature, and dilute aqueous amonia was added. A light yellow solid precipitated immediately. The mixture was

Table 3. Deviations of atoms from the mean-square ring planes in the molecule of 2-amino-5-phenyl-1,3,4-thiadiazole (**II**)

Atom	Deviation, Å	Atom	Deviation, Å
S^1	0.0024	C^1	–0.0043
N^2	0.0018	C^2	–0.0008
N^3	0.0036	C^3	0.0060
C^7	0.0045	C^4	–0.0060
C^8	0.0039	C^5	0.0008
$C^{1\,a}$	0.0311	C^6	0.0043
$N^{1\,a}$	0.0024	$C^{7\,a}$	–0.0557
$C^{6\,a}$	0.7440	$N^{1\,a}$	–0.7939
		$S^{1\,a}$	–0.9415

[a] These atoms were not included in the calculation of the corresponding plane.

Table 4. Hydrogen bond parameters in the structure of 2-amino-5-phenyl-1,3,4-thiadiazole (**II**)

Bond D–H···A	Position of atom A	Distance, Å			∠AHD, deg
		D···A	D···H	H···A	
N^1–H···N^2	$1-x$; $1-y$; $-z$;	2.974	0.914	2.068	170.7
N^1–H···N^3	x; $0.5-y$; $0.5+z$;	2.983	0.996	1.992	172.6

cooled, and the precipitate was filtered off, washed several times with hot ethanol, and dried in air. Yield 76%, mp 230–232°C. Crystals of **II** suitable for X-ray diffraction study were obtained by recrystallization from hot ethanol. Colorless crystals were thus obtained.

X-Ray analysis of single crystals of thiadiazole **II** was performed on an Enraf–Nonius CAD-4 automatic diffractometer ($\lambda \mathrm{Mo}K_\alpha$, graphite monochromator, $\Theta/2\Theta$-scanning to $2\Theta_{\max}$ 56°). The structure was solved by the Peterson method and was refined by the least-squares procedure in full-matrix approximation using SHELXL-93 program [7]; the final divergence factor was R 0.031 [from 1536 reflections with $F^2 > 2\sigma(I)$]. $C_8H_7N_3S$. Monoclinic crystals with the following unit cell parameters: $a = 11.085(3)$, $b = 7.544(3)$, $c = 11.180(3)$ Å; $\beta = 115.22(2)°$; $V = 845.8(5)$ Å^3; $d_{\mathrm{calc}} = 1.404$ g/cm^3; $\mu(\mathrm{Mo}K_\alpha) = 0.325$ mm^{-1}; $Z = 4$; space group $P2_1/c$.

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