

Crystalline and Molecular Structure of 2-Amino-5-phenyl-1,3,4-thiadiazole

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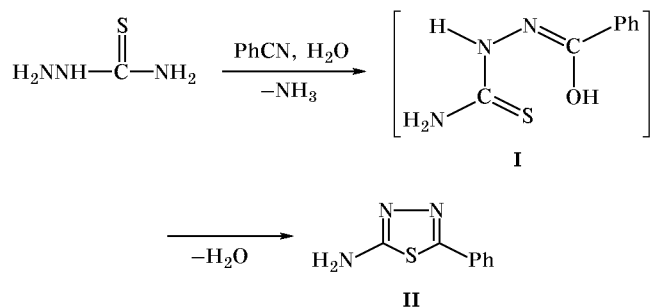
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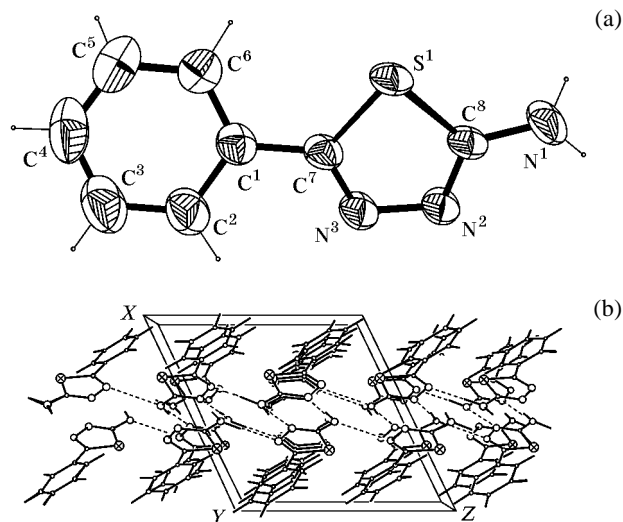
Abstract—The crystalline and molecular structure of 2-amino-5-phenyl-1,3,4-thiadiazole was studied by the X-ray diffraction method. C₈H₇N₃S. Monoclinic crystals: $a = 11.085(3)$, $b = 7.544(3)$, $c = 11.180(3)$ Å; $\beta = 115.22(2)^\circ$; $V = 845.8(5)$ Å³; $d_{\text{calc}} = 1.404$ g/cm³; $\mu(\text{MoK}\alpha) = 0.325$ 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 ¹H 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 trifluoroacetic 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

¹H NMR spectrum of **II** a triplet and two doublet signals from protons of the phenyl ring were present at δ 7.38, 7.66, and 7.73 ppm. The NH₂ 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**).

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^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)

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

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

Bond	<i>d</i> , \AA	Bond	<i>d</i> , \AA
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 ⁸ S ¹ C ⁷	86.88(13)	C ⁶ C ⁵ H ⁵	117(3)
C ⁶ C ¹ C ²	118.9(3)	C ¹ C ⁶ C ⁵	120.0(4)
C ⁶ C ¹ C ⁷	121.0(3)	C ¹ C ⁶ H ⁶	122(2)
C ² C ¹ C ⁷	120.0(3)	C ⁵ C ⁶ H ⁶	117(2)
C ³ C ² C ¹	120.4(4)	N ³ C ⁷ C ¹	124.0(3)
C ³ C ² H ²	127(2)	N ³ C ⁷ S ¹	113.3(2)
C ¹ C ² H ²	112(2)	C ¹ C ⁷ S ¹	122.6(2)
C ⁴ C ³ C ²	120.2(4)	C ⁷ N ³ N ²	113.7(2)
C ⁴ C ³ H ³	122(3)	C ⁸ N ² N ³	111.8(2)
C ² C ³ H ³	118(3)	N ² C ⁸ N ¹	123.6(3)
C ⁵ C ⁴ C ³	120.6(4)	N ² C ⁸ S ¹	114.3(2)
C ⁵ C ⁴ H ⁴	121(2)	N ¹ C ⁸ S ¹	122.1(2)
C ³ C ⁴ H ⁴	118(2)	C ⁸ N ¹ H ¹	119.5(17)
C ⁴ C ⁵ C ⁶	119.9(4)	C ⁸ N ¹ H ²	122(3)
C ⁴ C ⁵ H ⁵	123(3)	H ¹ N ¹ H ²	118(3)

Unshared electron pairs on the N¹ and S atoms in molecule **II** are conjugated with the C=N double bonds. This follows from the lengths of the N²-C⁸, N³-C⁷, N²-N³ bonds: 1.306(3), 1.296(3), and 1.383(3) \AA , 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 N¹ atom deviates from the mean-square plane of the heteroring by only 0.0024 \AA (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 \AA . The C¹-C⁷ bond which links the benzene and thiadiazole rings is appreciably extended [to 1.467(4) \AA]. 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^{1a}...N^{2b} and N^{1b}-H^{1b}...N^{2a}. The dimers in crystal are linked through intermolecular N-H...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 ¹H NMR spectra were obtained on XL-100 and XL-200 instruments using CD₃OD as solvent and HMDS as internal reference.

2-Amino-5-phenyl-1,3,4-thiadiazole (II) [5]. Tri-fluoroacetic 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 ammonia 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 (λ MoK α , 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 $F^2 > 2\sigma(I)$]. C₈H₇N₃S. Monoclinic crystals with the following unit cell parameters: $a = 11.085(3)$, $b = 7.544(3)$, $c = 11.180(3)$ Å; $\beta = 115.22(2)^\circ$; $V = 845.8(5)$ Å³; $d_{\text{calc}} = 1.404$ g/cm³; $\mu(\text{MoK}\alpha) = 0.325$ mm⁻¹; $Z = 4$; space group $P2_1/c$.

REFERENCES

- Sandstrom, J., *Adv. Heterocycl. Chem.*, 1969, vol. 9, pp. 165–177, 199–209.
- Ovsesyanyan, T.R., Gushoglyan, L.A., and Mirzoyan, V.S., *Arm. Khim. Zh.*, 1988, vol. 41, no. 3, pp. 136–142.
- Adam, F.A., *J. Chin. Chem. Soc.*, 1987, vol. 34, pp. 111–115.
- Eremin, K.I., Golovanov, A.V., Krutikov, V.I., and Lavrent'ev, A.N., *Russ. J. Gen. Chem.*, 1997, vol. 67, no. 1, pp. 138–140.
- Suzuki, N., Miwa, T., Aibara, S., Kanno, H., Takamori, H., Tsubokawa, M., Ryokawa, Y., Tsukada, W., and Isoda, S., *Chem. Pharm. Bull.*, 1992, vol. 40, no. 2, pp. 357–363.
- Nakamoto, K., *Infra-Red Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1963. Translated under the title *IK spektry neorganicheskikh i koordinatsionnykh soedinenii*, Moscow: Mir, 1966, pp. 204–206.
- Sheldrick, G.M., *SHELXL93. Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1993.