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CRYSTAL STRUCTURE OF 5-METHYL-N-PHENYL-1,3,4-THIADIAZOLE-2-AMINE

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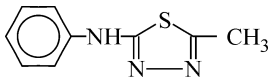
The crystal structure of 5-methyl-N-phenyl-1,3,4-thiadiazole-2-amine (I) is determined. The molecule of compound I is non-planar; the mean square plane of its phenyl cycle is located at an angle of 22.8°with respect to the planar thiadiazole fragment. The studied compound forms infinite chains in the crystal due to the translation along *a*, in which the molecules are bound by N–H…N and C–H…N bonds. Along with the van der Waals interaction, there is also a X–H…Cg (π ring) interaction between the chains in the crystal.

Keywords: thiadiazole, thiosemicarbazone of pyruvic acid, biological activity.

Thiadiazole derivatives are widely used as medications, chemical weed and pest killers, dyes, metal corrosion inhibitors, and ligands in coordination chemistry [1]. It is found that in many cases, their useful properties correspond well to the structure of these compounds. Thus, the synthesis and study of the structural parameters of new thiadiazole derivatives are of both scientific and practical interest.

The experiment has shown that on heating an alcoholic solution containing 4-phenylthiosemicarbazide and pyruvic acid in the 1:1 molar ratio, a compound of the composition $C_9H_9N_3S$ is formed in the reaction mixture, which is 5-methyl-N-phenyl-1,3,4-thiadiazole-2-amine (I).



(I)

Apparently, under these conditions the reaction between the initial compounds does not stop at the formation stage of 4-phenylthiosemicarbazone of pyruvic acid, but rather continues until decarboxylation and heterocyclization involving the sulfur atom and completes with the formation of I.

The aim of this work is to determine the structural parameters of thiadiazole I.

Experimental. Compound I has been obtained as follows: a solution containing 10 mmol of pyruvic acid in 10 ml of ethanol is added to the solution containing 10 mmol of 4-phenylthiosemicarbazide in 40 ml of ethanol under stirring and heating in a water bath (50-55°C). A light orange solution formed, which yielded a white fine crystalline precipitate on slow evaporation for one day (54% yield). This precipitate was filtered on a filter glass, washed with a small amount of ethanol, and dried in the air. Its composition was determined based on the elemental analysis. Found, % : C 56.40, H 4.59, N 21.90, and S 16.62. Calculated, % : C 56.52, H 4.74, N 21.97, and S 16.76.

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TABLE 1. Crystallographic Characteristics, Experimental and Refinement Data for Structure I

Formula	$C_9H_9N_3S$
Molecular weight	191.25
Temperature, K	293(2)
Radiation λ, Å	0.71069
Crystal symmetry system	Monoclinic
Space group	$P2_1/c$
Z	4
a, b, c, Å	6.010(1), 7.370(2), 20.560(4)
β, deg	93.43(3)
V, Å^3	909.0(3)
ρ_{calc}, g/cm^3	1.397
μ, mm^{-1}	0.308
F(000)	400
Crystal size, mm	0.23×0.20×0.15
θ range of data collection, deg	2.94-27.79
Ranges of reflection indices	$-7 \le h \le 7$, $-9 \le k \le 8$, $-26 \le l \le 22$
Measured reflections	7248
Independent reflections	2134 (R_{int} = 0.0765)
Reflections with $I > 2\sigma(I)$	1240
Refinement method	Full-matrix least squares method on F^2
Number of refined parameters	123
GOOF (all reflections)	1.003
R_1 ($I > 2\sigma(I)$)	R_1 = 0.0544
wR_2 (for all data)	wR_2 = 0.1633
Residual electron density (min/max). e/Å^3	0.425/–0.343

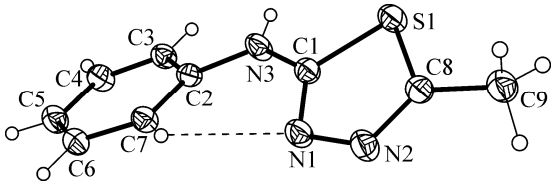

Fig. 1. Structure of molecule I.

Compound I dissolves well in dimethyl formamide and dimethyl sulfoxide, and on heating in water and alcohols. Its single crystals suitable for XRD were obtained by recrystallization of the substance under study from ethanol.

XRD was performed on a Nonius KappaCCD diffractometer (MoK_α radiation, graphite monochromator, room temperature). The measurement was performed by φ/ω-scanning. The structure of compound I was determined by the direct method and refined by the least squares method in the anisotropic approximation for non-hydrogen atoms using the SHELX-97 program [2]. Hydrogen atoms were refined in geometrically calculated positions, and their temperature factors U_H were taken to be 1.2 times that of carbon and nitrogen atoms bonded to them. The main parameters of the experiment, the determination and refinement of the structure are listed in Table 1, while some interatomic distances and bond angles are given in Table 2. Coordinates of the basal atoms of the studied structures have been deposited in the Cambridge Crystallographic Data Centre (CCDC 785085). Geometrical calculations and figures were performed using the PLATON program [3], in order to show structural packaging, only hydrogen atoms involved in hydrogen bonds were left (Fig. 1). In order to analyze the obtained structures, the data from the Cambridge Crystallographic Data Centre were used (version 5.30) [4, 5].

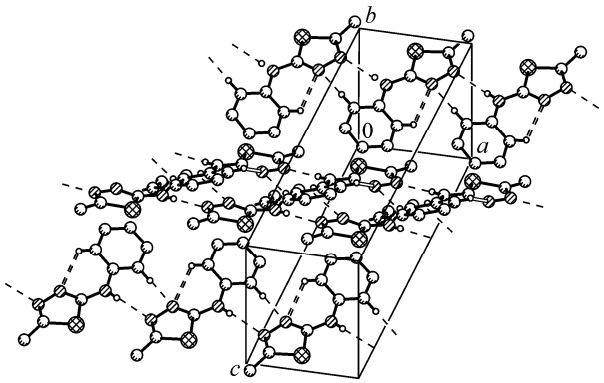

Fig. 2. Fragment of structure I.

TABLE 2. Interatomic Distances and Bond Angles for Compound I

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
S(1)–C(8)	1.729(3)	N(3)–C(1)	1.353(3)	C(4)–C(5)	1.384(4)
S(1)–C(1)	1.741(2)	N(3)–C(2)	1.415(3)	C(5)–C(6)	1.371(4)
N(1)–C(1)	1.309(3)	C(2)–C(3)	1.373(3)	C(6)–C(7)	1.394(3)
N(1)–N(2)	1.388(3)	C(2)–C(7)	1.392(3)	C(8)–C(9)	1.499(4)
N(2)–C(8)	1.291(3)	C(3)–C(4)	1.380(3)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
C(8)–S(1)–C(1)	87.5(1)	N(3)–C(1)–S(1)	120.5(2)	C(6)–C(5)–C(4)	119.2(2)
C(1)–N(1)–N(2)	111.8(2)	C(3)–C(2)–C(7)	119.1(2)	C(5)–C(6)–C(7)	121.0(2)
C(8)–N(2)–N(1)	114.0(2)	C(3)–C(2)–N(3)	117.8(2	C(2)–C(7)–C(6)	119.5(2)
C(1)–N(3)–C(2)	128.0(2)	C(7)–C(2)–N(3)	123.1(2)	N(2)–C(8)–C(9)	124.8(2)
N(1)–C(1)–N(3)	126.1(2)	C(2)–C(3)–C(4)	121.2(2)	N(2)–C(8)–S(1)	113.3(2)
N(1)–C(1)–S(1)	113.4(2)	C(3)–C(4)–C(5)	120.1(2)	C(9)–C(8)–S(1)	121.9(2)

TABLE 3. Geometrical Parameters of Hydrogen Bonds for Compound **I**

Bond D–H…A	*d*, Å			Angle D–H–A, deg	Symmetry operation
	D–H	H…A	D…A		
N3–H1…N2	0.77	2.31	3.089	178	–1+*x*, *y*, *z*
C3–H3…N1	0.93	2.49	3.342	152	–1+*x*, *y*, *z*
C7–H7…N1	0.93	2.39	2.965	119	*x*, *y*, *z*

Results and Discussion. The molecule of compound I is non-planar; the mean square plane of its phenyl cycle *A*(C(2)–C(7)) is oriented at an angle of 22.8° with respect to the planar *B*(S(1)N(1)N(2)C(1)C(8)) thiadiazole fragment, and the deviations of atoms from the above planes that they determine do not exceed 0.004 Å and 0.008 Å respectively. Nitrogen N(3) and carbon C(9) atoms lie almost in the thiadiazole ring plane, and their deviations from it are 0.008 Å and 0.001 Å. The occurrence of the methyl group in the thiazole fragment causes a decrease in the S(1)–C(8) bond length (1.729(3) Å) in comparison to that of 1,3,4-thiadiazole derivatives [7] (1.741(3) Å) and (1.752(4) Å) [8] by 0.013 Å and 0.023 Å respectively. Other interatomic distances in the cycle agree with those described in the literature.

Compound I forms infinite chains in the crystal due to the translation along *a*, in which the molecules are bound by N–H…N and C–H…N bonds. However, there is also an intramolecular C(7)–H(7)…N(1) hygrogen bond (Fig. 2, Table 3). Along with the van der Waals interaction, there is also a X–H…Cg (π ring) interaction between the chains in the crystal

(H Cg < 3.0 Å, γ < 30.0°, where γ is the angle between the HCg vector and the normal to the aromatic ring [3]). Thus, for the C(6)–H(6)…Cg(A) interaction the distance between the H(6) atom and *A* centroid is 2.83 Å, while the angle γ is 9.0°.

Hence, the study has shown that the condensation reaction of 4-phenylthiosemicarbazide with pyruvic acid in hot ethanol does not end with the formation of 4-phenylthiosemicarbazone of pyruvic acid, but continues until decarboxylation and heterocyclization involving the sulfur atom, and is complete with the formation of 5-methyl-N-phenyl-1,3,4-thiadiazole-2-amine.

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