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MOLECULAR AND CRYSTAL STRUCTURE OF 5-AMINO-3-(N-*p*-METHYLBENZOYL-N-*p*-TOLUENESULFONYL)AMINO-1-PHENYL-1,2,4-TRIAZOLE

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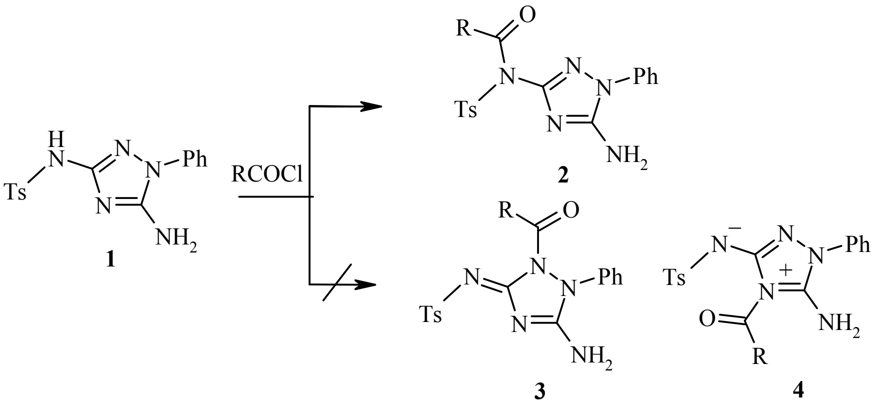
It has been established by X-ray structural analysis that the initial product of the interaction of 5-amino-1-phenyl-3-p-toluenesulfonylamino-1,2,4-triazole with p-methylbenzoyl chloride is 5-amino-3-(N-p-methylbenzoyl-N-p-toluenesulfonyl)amino-1-phenyl-1,2,4-triazole.

Keywords: amino- and 3,5-diamino-1,2,4-triazole, 5-amino-3-(N-*p*-methylbenzoyl-N-*p*-toluenesulfonyl)-amino-1-phenyl-1,2,4-triazole, 1,2,4-triazole, acylation, X-ray structural analysis.

3,5-Diamino-1-R-1,2,4-triazoles enter into the composition of medicinal preparations [1] and are used for obtaining substances possessing a wide spectrum of biological activity [2, 3]. On acylating 5-amino-1-phenyl-3-*p*-toluenesulfonylamino-1,2,4-triazole (**1**) with *p*-methylbenzoyl chloride in acetonitrile in the presence of pyridine a compound is obtained which, on the basis of data of elemental analysis, IR and NMR spectroscopy, was assigned the structure of 5-amino-3-(N-*p*-methylbenzoyl-N-*p*-toluenesulfonyl)amino-1-phenyl-1,2,4-triazole (**2**) [4]. However the spectral data presented in [4] were not able completely to exclude the possibility of isomeric structures of this compound, such as structures **3** and **4**.



1 **2** **3** **4**

R = p-MeC$_6$H$_4$

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Since the structure of the obtained compound enables the special features of the acylation reactions of 3-acylamino-5-amino- and 5-amino-3-sulfonylamino-1-R-1,2,4-triazoles to be understood [4], we have carried out an X-ray structural analysis of it.

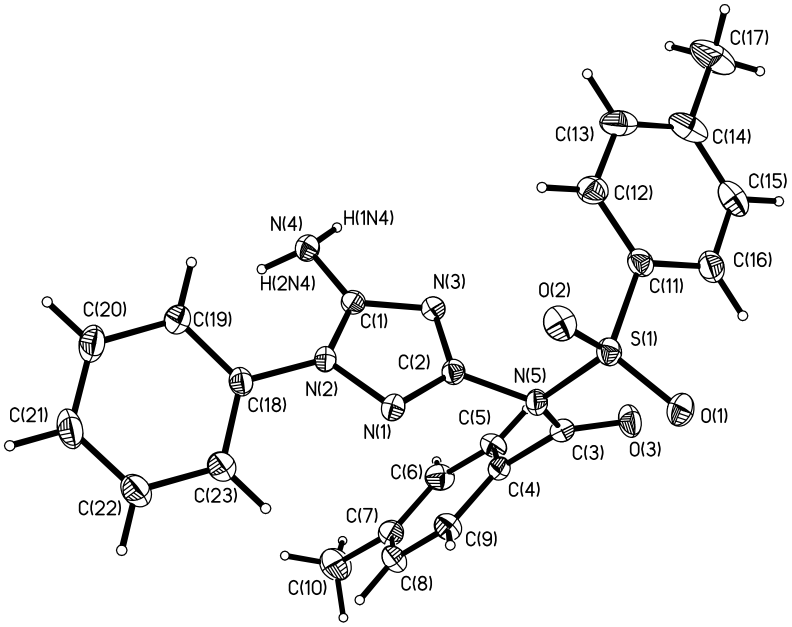

Fig. 1. Structure of the compound **2** molecule.

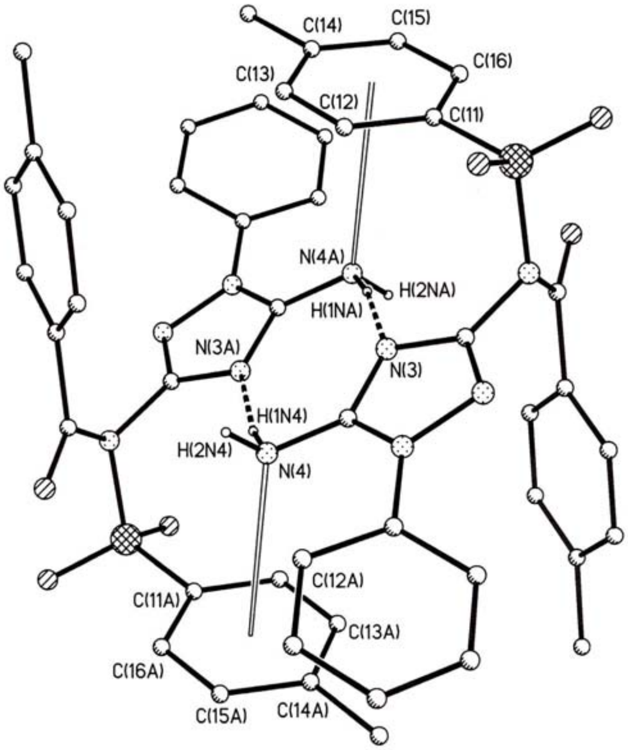

Fig. 2. System of intermolecular hydrogen bonds in the crystal of compound **2**.

According to the data of X-ray structural analysis (Figs. 1, 2, Tables 1, 2) the compound **2** molecule has a non-planar structure. The phenyl group makes a dihedral angle of 29.4° with the plane of the triazole ring, and the benzene rings of the *p*-methylbenzoyl and *p*-toluenesulfonyl groups are inclined to the triazole ring at 50.1 and 28.6° respectively.

The bond lengths in the triazole ring are in agreement with the corresponding values of substituted triazoles studied previously [3, 5-11]. The $N_{(4)}$ and $N_{(5)}$ atoms have a trigonal pyramidal configuration (sum of valence angles 336.2 and 350.5° respectively). The deviation of the $N_{(4)}$ atom from the plane of the triazole ring is 0.014(3) Å, while the $N_{(5)}$ atom deviates by 0.091(3) Å, probably as a result of the reduced intramolecular contact $C_{(2)}\cdots C_{(9)}$ of 3.05 Å and the shortened contacts at $N_{(1)}\cdots C_{(9)}$ of 3.18 and $N_{(3)}\cdots C_{(4)}$ 3.19 Å.

The $C_{(1)}–N_{(4)}$ bond length (1.360(2) Å) is in agreement with corresponding values in other 5-amino-1,2,4-triazoles (1.347-1.371 Å [5-7]). The $C_{(2)}–N_{(5)}$ bond (1.423(2) Å) is lengthened in comparison with 3-amino-1,2,4-triazoles, in which it is 1.370-1.376 Å [3, 9-11], and is closest to the analogous bond in 1-(1-methyl-5-morpholino-1,2,4-triazol-3-yl)-3-phenyl-2-thioxoimidazolidine-4,5-dione (1.429 Å) [8], in which the 3-amino group of the 1,2,4-triazole is included in an imidazolidine ring.

The system of atoms formed by the carbonyl group, the $N_{(5)}$ atom, and the sulfonyl group ($O_{(3)}–C_{(3)}–N_{(5)}–S_{(1)}–O_{(1)}–O_{(2)}$) is close in geometric parameters to the corresponding segment in N-tolyl-N-tosyl-*p*-chlorobenzamide [12]. The bond length of $C_{(3)}–N_{(5)}$ is 1.429(2), $S_{(1)}–N_{(5)}$ 1.706(1) Å (1.418 and 1.704 Å respectively [12]), the angles $O_{(3)}C_{(3)}N_{(5)}$ 121.2(2), $C_{(3)}N_{(5)}S_{(1)}$ 119.1(1), $O_{(1)}S_{(1)}N_{(5)}$ 106.16(7), $O_{(1)}S_{(1)}O_{(2)}$ 120.77(8)° (121.3, 118.4, 107.1, 119.5° [12]), the carbonyl group is almost coplanar with the $S_{(1)}–O_{(2)}$ bond, the

TABLE 1. Some Bond Lengths (*d*) in Compound **2**

Bond	*d*, Å	Bond	*d*, Å
$N_{(1)}–C_{(2)}$	1.301(2)	$N_{(5)}–C_{(3)}$	1.429(2)
$N_{(1)}–N_{(2)}$	1.388(2)	$O_{(3)}–C_{(3)}$	1.208(2)
$N_{(2)}–C_{(1)}$	1.366(2)	$S_{(1)}–N_{(5)}$	1.706(1)
$N_{(3)}–C_{(1)}$	1.328(2)	$S_{(1)}–O_{(1)}$	1.426(1)
$N_{(3)}–C_{(2)}$	1.357(2)	$S_{(1)}–O_{(2)}$	1.428(1)
$N_{(4)}–C_{(1)}$	1.360(2)	$S_{(1)}–C_{(11)}$	1.757(2)
$N_{(5)}–C_{(2)}$	1.423(2)	$C_{(3)}–C_{(4)}$	1.490(2)
$N_{(2)}–C_{(18)}$	1.424(2)		

TABLE 2. Some Valence Angles (ω) in Compound **2**.

Angle	ω,deg	Angle	ω, deg
$C_{(2)}N_{(1)}N_{(2)}$	101.1(1)	$H_{(1N4)}N_{(4)}H_{(2N4)}$	115.6
$C_{(1)}N_{(2)}N_{(1)}$	109.3(1)	$C_{(2)}N_{(5)}C_{(3)}$	115.7(1)
$C_{(1)}N_{(3)}C_{(2)}$	102.2(1)	$C_{(2)}N_{(5)}S_{(1)}$	115.7(1)
$N_{(1)}C_{(2)}N_{(3)}$	117.7(1)	$C_{(3)}N_{(5)}S_{(1)}$	119.1(1)
$N_{(3)}C_{(1)}N_{(2)}$	109.8(1)	$O_{(3)}C_{(3)}N_{(5)}$	121.2(2)
$C_{(1)}N_{(2)}C_{(18)}$	130.4(1)	$O_{(3)}C_{(3)}C_{(4)}$	123.9(2)
$N_{(1)}N_{(2)}C_{(18)}$	119.9(1)	$N_{(5)}C_{(3)}C_{(4)}$	115.0(1)
$N_{(1)}C_{(2)}N_{(5)}$	122.9(1)	$O_{(1)}S_{(1)}O_{(2)}$	120.77(8)
$N_{(3)}C_{(2)}N_{(5)}$	119.3(1)	$O_{(1)}S_{(1)}N_{(5)}$	106.16(7)
$N_{(3)}C_{(1)}N_{(4)}$	124.0(2)	$O_{(2)}S_{(1)}N_{(5)}$	103.92(7)
$N_{(4)}C_{(1)}N_{(2)}$	126.2(1)	$O_{(1)}S_{(1)}C_{(11)}$	109.73(8)
$C_{(1)}N_{(4)}H_{(1N4)}$	108.9	$O_{(2)}S_{(1)}C_{(11)}$	108.09(8)
$C_{(1)}N_{(4)}H_{(2N4)}$	111.6	$N_{(5)}S_{(1)}C_{(11)}$	107.30(7)

fragment $O_{(3)}C_{(3)}N_{(5)}S_{(1)}O_{(2)}$ is planar within the limits ±0.02 Å, and the pseudotorsion angle $O_{(3)}C_{(3)}S_{(1)}O_{(2)}$ is 174.9° (178.4° [12]). It should be noted that in compound **2** the $N_{(5)}$–$S_{(1)}$ bond length is greater than the length characteristic of N-acyl-N-tosylamino fragments (1.60-1.64 Å) [13]. The same S–N bond length is found only in two more molecules containing the fragment under consideration [14, 15].

In the crystal, molecules are combined in centrosymmetric H-dimers (Fig. 2) as a result of a hydrogen bond $N_{(3)}\cdots H_{(1NA)}–N_{(4A)}$ [parameters of the hydrogen bond are length $N_{(3)}\cdots N_{(4A)}$ 3.016(2), $N_{(3)}\cdots H_{(1NA)}$ 2.14 Å, angle $N_{(3)}\cdots H_{(1NA)}–N_{(4A)}$ 171°). In addition, in the dimer a second interaction was observed of the unshared pair of the $N_{(4)}$ atom and the π-system of the ring $C_{(11A)}$–$C_{(16A)}$ and correspondingly of the $N_{(4A)}$ atom and the π-system of the ring $C_{(11)}$–$C_{(16)}$. The distance $N_{(4)}\cdots$centroid ($C_{(11A)}$–$C_{(16A)}$) is equal to 3.284 Å.

The X-ray structural analysis data therefore confirmed the proposed direction of the acylation reaction of 3-acylamino-5-amino- and 5-amino-3-sulfonylamino-1-R-1,2,4-triazoles [4]. Acylation of the substituted 3-amino group initially is confirmed by the formation of 5-amino-3-(N,N-diacyl)amino- or 5-amino-3-(N-acyl-N-sulfonyl)amino-1-R-1,2,4-triazoles, which are then rearranged to the thermodynamically more stable 3,5-diacylamino- or 5-acylamino-3-sulfonylamino-1-R-1,2,4-triazoles.

EXPERIMENTAL

X-ray Structural Investigation. Colorless prismatic crystals of compound **2**, obtained from a DMF–EtOH, 1 : 1 mixture, were monoclinic, $C_{23}H_{21}N_5O_3S$. At 120 K a = 8.1186(6), b = 18.204(1), c = 14.666(1) Å, β = 94.203(2)°, V = 2161.7(3) Å^3, M_r = 447.51, Z = 4, space group $P2_1/c$, d_{calc} = 1.375 g/cm^3. The experimental collection of 13461 reflections was obtained on a Bruker SMART CCD area detector diffractometer at 120 K (λMoKα radiation, $2\theta_{max}$ = 54.00°) with a monocrystal of size 0.50×0.40×0.35 mm. After averaging equivalent reflections 5814 independent reflections were obtained (R_{int} = 0.0448), which were used to decipher and refine the structure. Absorption (μ = 0.186 mm^{-1}) was not taken into consideration.

The structure was solved by the direct method, all the non-hydrogen atoms were localized in electron density difference syntheses and refined on F^2_{hkl} in an anisotropic approach. The hydrogen atoms of the NH_2 group were localized in electron density difference syntheses and refined by the riding model isotropic approach; H(C) hydrogen atoms were placed in geometrically calculated positions and moved on refining in the rider model with $U(H) = nU(C)$, where n = 1.2 and 1.5 for CH and CH_3 groups respectively, $U(C)$ is the equivalent temperature factor of the carbon atom to which the corresponding H atom is linked.

Final values of the uncertainty factors: R_1 = 0.0436 (calculated on F_{hkl} for 3766 reflections with $I > 2\sigma(I)$), wR_2 = 0.1016 (calculated on F^2_{hkl} for all 4534 reflections), GOOF = 1.004, 289 refined parameters.

All calculations were carried out with the SHELXTL PLUS 5 set of programs [16].

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