

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF 1-(DIPHENYLMETHYLENE)-2-(THIAZOLO[4,5-b]PYRIDIN-2-YL)HYDRAZINE

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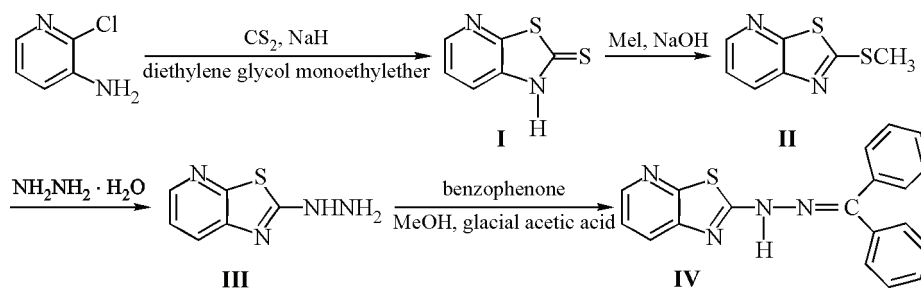
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The 1-(diphenylmethylene)-2-(thiazolo[4,5-b]pyridin-2-yl)hydrazine compound (**IV**) is synthesized based on 3-amino-2-chloropyridine precursor and characterized by single crystal X-ray diffraction. The structural analysis reveals that compound **IV** belongs to the monoclinic system, space group $P2_1/c$, $a = 11.869(5) \text{ \AA}$, $b = 13.155(6) \text{ \AA}$, $c = 10.970(5) \text{ \AA}$, $\beta = 102.431(5)^\circ$, $V = 1672.6(12) \text{ \AA}^3$, $Z = 4$. In the crystal structure, the molecular species are linked by intermolecular $\text{N—H}\cdots\text{N}$ hydrogen bonds into one-dimensional chains.

Keywords: 1-(diphenylmethylene)-2-(thiazolo[4,5-b]pyridin-2-yl)hydrazine, synthesis, crystal structure, $\text{N—H}\cdots\text{N}$ hydrogen bond.

Hydrazone derivatives are an emerging class of materials, which have been demonstrated to possess a wide range of bioactivities such as antimicrobial [1], anticonvulsant [2], antifungal [3], anticancer [4], antitubercular [5], antiviral [6], and antibacterial [7]. Meanwhile, hydrazones have also interesting ligation properties because of the presence of several coordination sites, and thus their metal complexes are important for their possible biological applications [8, 9]. In addition, hydrazone derivatives containing heterorings such as pyridine [10], thiazole [11], and pyrazole [12] rings have recently attracted special attention. For example, a series of benzothiazolyl hydrazones and their complexes have been reported for their bioactivities [13–16]. However, in order to improve the water solubility and the coordination abilities with metal ions of benzothiazolyl hydrazones, we have attempted to replace the benzene ring moieties in these compounds by nitrogen heterocycles such as pyridine, pyrimidine, pyridazine, and pyrazine. This paper presents the results of the synthesis and single crystal X-ray diffraction analysis of a novel hydrazone compound containing the pyridothiazole ring: 1-(diphenylmethylene)-2-(thiazolo[4,5-b]pyridin-2-yl)hydrazine (**IV**).



Scheme 1

Experimental. Compound **IV** was obtained from a 3-amion-2-chloropyridine precursor (Scheme 1), which is referred to the reported procedure [13]. Single crystals suitable for X-ray diffraction were obtained by crystallization of compound **IV** from methanol, and the results were as follows:

Compound **I**: Yield: 45 %. $T_m = 274\text{--}276$ °C. Anal. Calcd. (%) for $C_6H_4N_2S_2$: C, 42.83; H, 2.40; N, 16.65. Found (%): C, 42.69; H, 2.33; N, 16.78. IR (KBr, cm^{-1}): 3119 (NH), 1393 (C=S). 1H NMR (DMSO, 400 MHz) δ : 13.93 (s, 1H, NH), 8.40 (d, 1H, ArH), 7.61 (d, 1H, ArH), 7.41 (t, 1H, ArH).

Compound **II**: Yield: 92 %. $T_m = 82\text{--}84$ °C. Anal. Calcd. (%) for $C_7H_6N_2S_2$: C, 46.13; H, 3.32; N, 15.37. Found (%): C, 46.19; H, 3.25; N, 15.46. IR (KBr, cm^{-1}): 2985 (CH_3). 1H NMR ($CDCl_3$, 400 MHz) δ : 8.44 (d, 1H, ArH), 8.05 (d, 1H, ArH), 7.34 (t, 1H, ArH), 2.80 (s, 3H, CH_3).

Compound **III**: Yield: 85 %. $T_m = 240\text{--}242$ °C. Anal. Calcd. (%) for $C_6H_6N_4S$: C, 43.36; H, 3.64; N, 33.71. Found (%): C, 43.50; H, 3.61; N, 33.83. IR (KBr, cm^{-1}): 3325, 3302 (NH_2), 3196 (NH). 1H NMR (DMSO, 400 MHz) δ : 9.34 (s, 1H, NH), 8.07 (d, 1H, ArH), 7.58 (d, 1H, ArH), 7.21 (t, 1H, ArH), 5.14 (s, 2H, NH_2).

Compound **IV**: Yield: 30 %. $T_m = 178\text{--}180$ °C. Anal. Calcd. (%) for $C_{19}H_{14}N_4S$: C, 69.07; H, 4.27; N, 16.96. Found (%): C, 68.92; H, 4.22; N, 16.83. IR (KBr, cm^{-1}): 3331 (NH), 1597 (C=N). 1H NMR (DMSO, 400 MHz) δ : 11.84 (s, 1H, NH), 8.15 (s, 1H, ArH), 7.42 (m, 5H, Ar—H), 7.26 (m, 7H, Ar—H).

The X-ray diffraction analysis of compound **IV** was performed on a Bruker SMART APEX II CCD diffractometer with a graphite monochromated MoK_{α} radiation source ($\lambda = 0.71073$ Å). The intensity data were collected at room temperature using the ω -2 θ scan technique. The data were corrected for the Lorentz polarization factor and absorption. The structures were solved by direct methods with SHELXS-97 and expanded using Fourier techniques [17]. All H atoms were refined in the isotropic approximation with U_{iso} equal to $1.2U_{eq}$ of the adjacent C or N atoms respectively. A summary of the crystal structure parameters, data collection, structure determination and refinement is provided in Table 1. CIF files containing complete information on the structure of **IV** was deposited with the Cambridge Crystallographic Data Center (no. 883380); the file is freely available upon request from the following web site: http://www.ccdc.cam.ac.uk/data_request/cif.

Table 1

Crystallographic data and refinement details for compound **IV**

| | |
|-------------------------------------|------------------------------------|
| Empirical formula | $C_{19}H_{14}N_4S$ |
| Molecular weight | 330.40 |
| Crystal system | Monoclinic |
| Space group | $P2(1)/c$ |
| $a, b, c, \text{Å}$ | 11.869(5), 13.155(6), 10.970(5) |
| β , deg. | 102.431(5) |
| $V, \text{Å}^3$ | 1672.6(12) |
| Z | 4 |
| $d_{calc}, g/cm^3$ | 1.312 |
| μ, mm^{-1} | 0.200 |
| Crystal size, mm | 0.41×0.32×0.25 |
| θ , deg. | 2.34—25.50 |
| Reflections collected / unique | 10588 / 3105 [$R(int) = 0.0694$] |
| GOOF on F^2 | 1.040 |
| R factors ($I > 2\sigma(I)$) | $R_1 = 0.0572, wR_2 = 0.1218$ |
| R factors (all data) | $R_1 = 0.1071, wR_2 = 0.1432$ |
| Residual extrema, $e/\text{Å}^{-3}$ | 0.284 / -0.388 |

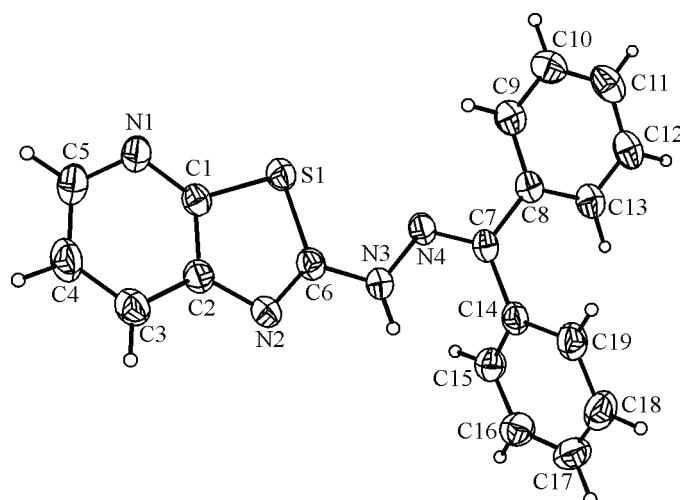


Fig. 1. Molecular structure of compound **IV**

Results and discussion. The molecular structure of compound **IV** is shown in Fig. 1. The independent part of the unit cell contains one molecule of compound **IV**, which is constructed by the pyridine-thiazole moiety, the hydrazone linker, and the biaryl moiety. The bond lengths and bond angles in the structure of **IV** are typical of the compounds of this class [14]. The C(1)—N(1), C(5)—N(1), C(2)—N(2), and C(6)—N(2) bond lengths are 1.334(3) Å, 1.336(4) Å, 1.376(3) Å, and 1.298(3) Å respectively, which are typical of azocompounds. The C(6)—N(3), N(3)—N(4), and C(7)—N(4) bond lengths are 1.369(3) Å, 1.373(3) Å, and 1.297(3) Å respectively, which is observed in similar compounds [18]. The C(1)—S(1) and C(6)—S(1) bond lengths of 1.746(3) Å and 1.747(3) Å are intermediate between the double (~1.56 Å) and single (~1.82 Å) bonds. The shortening of the C—S bonds shows the partial double-bond character of the C—S bonds, which agrees with the literature data [14]. The C(1)—S(1)—C(6) angle is 87.11(13)°, which is smaller than that in simple thiazoles. The pyridine-thiazole heterocyclic ring (P1) is nearly parallel to one benzene ring C8—C13 (P2), but perpendicular to another benzene ring C14—C19 (P3). The P1/P2, P1/P3, and P2/P3 dihedral angles are 12.17(8)°, 80.36(6)°, and 77.16(9)° respectively. The N3, N4, C7, C8, and C14 atoms lie in the same plane that is almost coplanar with P1 and P2.

In the crystal, the adjacent molecules form one-dimensional chains along the *c* axis by means of intermolecular H-bonds: N(3)—H(3)⋯N(1) (*x*, $-y+1/2$, $z-1/2$) (N⋯N 2.853(3) Å, H⋯N 2.08 Å, N—H⋯N angle 149.7°), as shown in Fig. 2.

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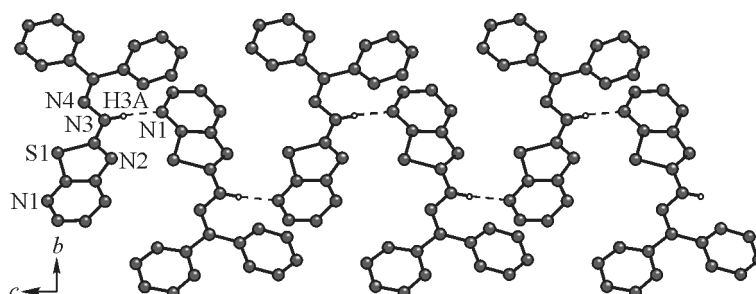


Fig. 2. H-bonded 1D chains of the molecules of compound **IV** (hydrogen bonds are shown by dashed lines, some hydrogen atoms are omitted for clarity)

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