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Synthesis and Crystal Structure of 4-Phenyl-3-(pyridin-4-yl)-1*H*-1,2,4-triazole-5(4*H*)-thione

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A triazole derivative *i.e.*, 4-phenyl-3-(pyridin-4-yl)-1*H*-1,2,4-triazole-5(4*H*)-thione was synthesized and its structure was studied by X-ray diffraction. The crystals are orthorhombic, space group pbcn with a = 11.337 (2), b = 12.789 (3), c = 17.625 (4) Å, α = 90.00, β = 90, γ = 90°, V = 2555.4 (9) Å^3, Z = 8, F(000) = 1056, D_c = 1.322 g/cm^3, μ = 0.240 cm^{-1}, the final R = 0.0528 and wR = 0.1429. A total of 19773 reflections were collected, of which 2254 were independent (R_{int} = 0.043).

Keywords: Synthesis, Heterocycle, Crystal structure, Triazole.

INTRODUCTION

In recent years, sulfur and nitrogen linked heterocyclic compounds have received special attention due to their pesticidal importance[1]. 1,2,4-Triazole moiety has been claimed to have beneficial medicinal and agricultural applications[2]. Because of its good bioactivity and usefulness as intermediates in organic synthesis, the 1,2,4-triazole has been widely studied[3]. Meanwhile, some triazole and nicotine structure are also exhibited good biological activity[4]. As a continuation of our work, a triazole derivative have been synthesized and its structure was confirmed by X-ray crystallography. In this paper, we report the synthesis and crystal structure of the 4-phenyl-3-(pyridin-4-yl)-1*H*-1,2,4-triazole-5(4*H*)-thione.

EXPERIMENTAL

Synthesis: Compound nicotine acylhydrazine reacting with 1.5 g of isothiocyanate gave compound thiurea after 3h refluxing in alcohol. Compound thiourea was refluxed with 2 N NaOH for 3 h and was neutralized by diluted hydrochloric acid to give title compound. The yields of this step were quantitative. The compound was recrystallized by DMF, to give colorless prism.

The crystal of title compound with dimensions of 0.18 mm × 0.16 mm × 0.10 mm was mounted on a Rigaku Saturn CCD area-detector diffractometer with a graphite-monochromated MoKα radiation (γ = 0.71073 Å) by using a phi and scan modes at 293 (2) K in the range of 2.31° ≤ θ ≤ 25.02°. The crystal belongs to monoclinic system with space group $P2_1/c$ and crystal parameters of a = 11.337 (2) Å, b = 12.789 (3) Å, c = 17.625 (4) Å, α = 90°, β = 90°, γ = 90°, V = 2555.4 (9) Å^3, D_c = 1.322 g/cm^3. The absorption coefficient μ = 0.240 mm^{-1} and Z = 8. The structure was solved by direct methods with SHELXS-97[5] and refined by the full-matrix least squares method on F^2 data using SHELXL-97[6]. The empirical absorption corrections were applied to all intensity data. H atom of N-H was initially located in a difference Fourier map and were refined with the restraint Uiso (H) = 1.2 Ueq(N). Other H atoms were positioned geometrically and refined using a riding model, with d(C···H) = 0.93-0.97 Å and Uiso (H) = 1.2 Ueq (C) or 1.5 Ueq (Cmethyl). The final full-matrix least squares refinement gave R = 0.0528 and wR = 0.1429.

RESULTS AND DISCUSSION

Structure of the title complex: The title compound was confirmed by single crystal X-ray diffraction analysis. Crystallographic and refinement parameters are given in Table-1. The selected bond lengths and bond angles listed in Tables 2-4, respectively. The structure was solved by direct methods. Anisotropic displacement parameters were applied to all nonhydrogen atoms in full-matrix least-square refinements based on F_2. The hydrogen atoms were set in calculated positions with a common fixed isotropic thermal parameter.

The molecular structure and the packing view of the title compound are shown in Figs. 1 and 2, respectively.

The title compound crystallizes in the orthorhombic space group pbcn. The unit cell contains one molecule of $C_{13}H_{10}N_4S$. As can be seen in Fig. 1, the H atom of the NH group is transferred to the thio group of triazole ring. The dihedral angles

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE TITLE COMPOUND

Items	Values
Empirical formula	$C_{13}H_{10}N_4S$
Formula weight	254.31
Crystal system	Orthorhombic
Unit cell dimensions	
a (Å)	11.337(2)
b (Å)	12.789(3)
c (Å)	17.625(4)
Unit cell angles (°)	
α	90
β	90
γ	90
Volume (Å^3)	2555.4(9)
Z	8
Temperature (K)	293(2)
Space group	Pbcn
Wavelength (Å)	0.71073
Calculated density (g/cm^3)	1.322
Absorption coefficient (mm^{-1})	0.240
F(000)	1056
Crystal size (mm)	0.18 × 0.16 × 0.10
Theta range for data collection (°)	2.31 – 25.02
Reflections collected	19773
Independent reflections	2254 [$R_{(int)}$ = 0.0430]
Final R indices [I > 2σ(I)]	R_1 = 0.0528, wR_2 = 0.1429

between the triazole ring and pyridine or phenyl planes are 37.2° and 121.5°, respectively. The rings (C1, C2, C3, C4, C5, N1), (C6, C7, N2, N3, N4) and (C8, C9, C10, C11, C12, C13) are fairly planar with plane equation 10.755x + 3.350y + 3.121z = 5.9519 and 10.627x + (-4.453)y + (-0.193)z = -0.4902, -7.131x + (-2.781)y + 13.155z = 11.4557, respectively. The largest deviation from the least squares plane is 0.0087 Å7.

As shown in Fig. 2, the crystal structure is stabilized by van der Waals' interactions.

TABLE-2
SELECTED BOND LENGTHS [Å] FOR THE TITLE COMPOUND

Bond lengths	X-ray Crystal
S(1)-C(7)	1.668(2)
N(1)-C(3)	1.331(3)
N(1)-C(2)	1.335(3)
N(2)-C(6)	1.301(3)
N(2)-N(3)	1.381(2)
N(3)-C(7)	1.346(3)
N(4)-C(6)	1.387(3)
N(4)-C(7)	1.391(3)
N(4)-C(8)	1.445(3)
C(1)-C(5)	1.385(3)

TABLE-3
SELECTED BOND ANGLES [°] FOR THE TITLE COMPOUND

Bond angles	X-ray Crystal
C(3)-N(1)-C(2)	117.2(2)
C(6)-N(2)-N(3)	104.36(17)
C(7)-N(3)-N(2)	113.40(17)
C(6)-N(4)-C(7)	107.31(17)
C(6)-N(4)-C(8)	127.07(17)
C(7)-N(4)-C(8)	125.08(17)
C(5)-C(1)-C(2)	118.6(2)
N(1)-C(2)-C(1)	123.5(2)

TABLE-4
SELECTED TORSIONAL ANGELS (°)
FOR THE TITLE COMPOUND

Bond angles	X-ray Crystal
C(3)-N(1)-C(2)-C(1)	2.3(4)
N(1)-C(3)-C(4)-C(5)	-0.9(4)
N(3)-N(2)-C(6)-N(4)	0.3(2)
C(7)-N(4)-C(6)-N(2)	-0.1(2)
C(8)-N(4)-C(6)-N(2)	171.78(19)
C(7)-N(4)-C(6)-C(5)	178.7(2)
C(1)-C(5)-C(6)-N(2)	141.3(2)
C(4)-C(5)-C(6)-N(4)	144.8(2)

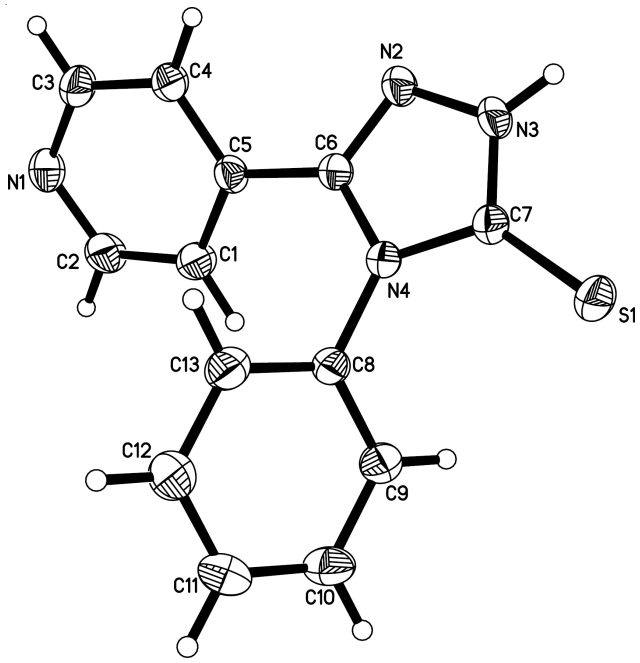

Fig. 1. Molecular structure of the title compound

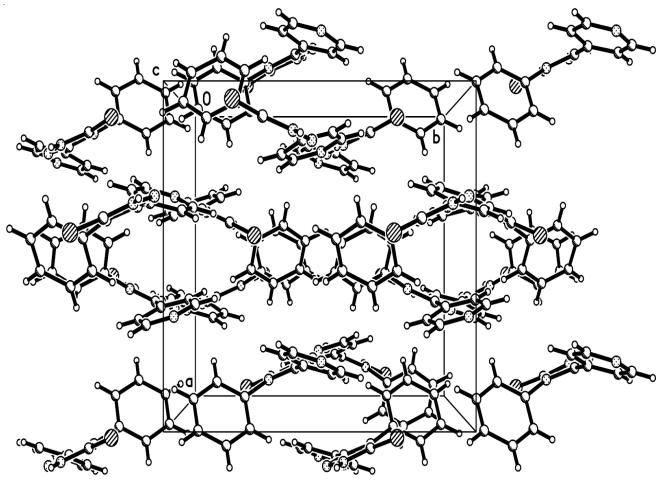

Fig. 2. Two-dimensional network of the title compound

Supplementary material: CCDC 955581 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge CrystallographicData Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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