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Key indicators

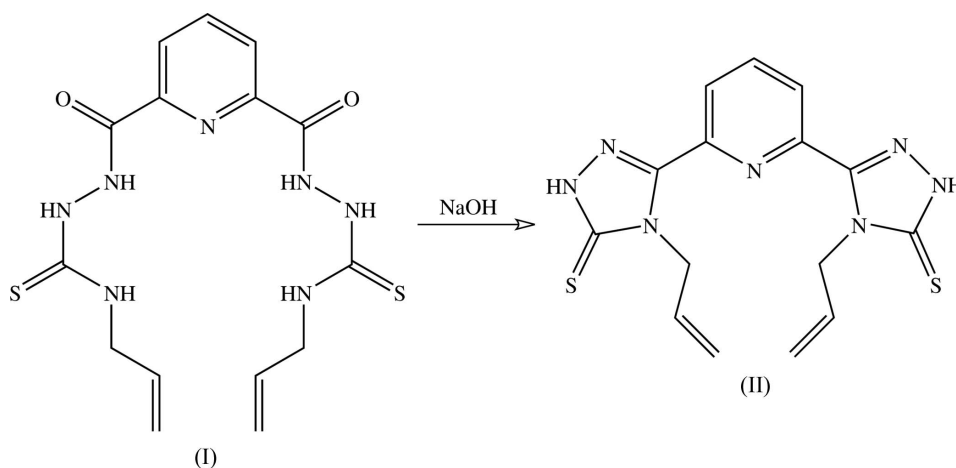
Single-crystal X-ray study
 $T = 296$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
 R factor = 0.051
 wR factor = 0.147
Data-to-parameter ratio = 15.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

3,3'-(Pyridine-2,6-diyl)bis(4-allyl-4,5-dihydro-1H-1,2,4-triazole-5-thione)

In the title compound, $\text{C}_{15}\text{H}_{15}\text{N}_7\text{S}_2$, the asymmetric unit consists of two independent molecules which differ from each other in the orientation of the allyl group. In each molecule, there are two very weak intramolecular $\text{C}-\text{H} \cdots \text{N}$ hydrogen bonds. In the crystal structure, the two independent molecules are arranged alternately through $\text{N}-\text{H} \cdots \text{S}$ hydrogen-bonded rings to form a molecular chain running along the $[12\bar{1}]$ direction.

Comment

1,2,4-Triazoles and their derivatives represent one of the most biologically active classes of compounds, possessing a wide spectrum of activities including antibacterial, antifungal, antiviral, anti-inflammatory, anticonvulsant, antidepressant, antihypertensive, analgesic and hypoglycaemic properties (Abbas & Khalil, 2005; Holla *et al.*, 1998). Carboxylic acid hydrazides are condensed with carbon disulfide in ethanolic potassium hydroxide to yield the potassium 3-aryldithiocarbazates, which are cyclized with hydrazine to the triazoles (Cansız *et al.*, 2004; Reid & Heindel, 1976). In addition, there are some studies of electronic structures and thiol–thione tautomeric equilibrium of heterocyclic thione derivatives (Koparır *et al.*, 2005; Coynan *et al.*, 2002). In view of these important properties, the present single-crystal X-ray diffraction study of the title compound, (II), was carried out.



The asymmetric unit of (II) contains two crystallographically independent molecules, denoted *A* (atoms S1/S2/N1–N7/C1–C15) and *B* (atoms S3/S4/N8–N14/C16–C30) (Fig. 1). The molecule of (II) contains three bonded planar rings, which are not coplanar with each other. In molecule *A*, the central pyridine ring makes dihedral angles of 10.9 (2) and

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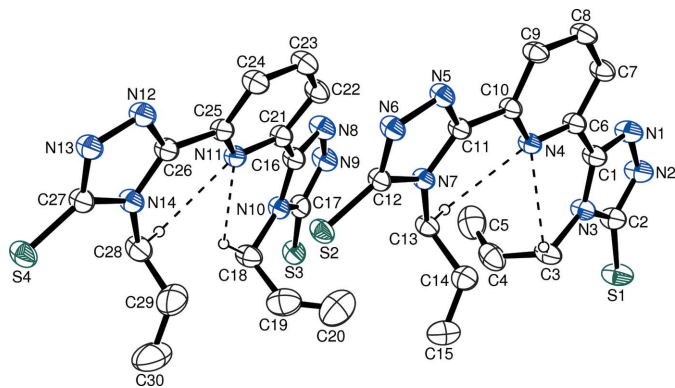


Figure 1

The two crystallographically independent molecules of (II), showing 30% probability displacement ellipsoids and the atom-numbering scheme. Intramolecular C—H...N contacts are represented by dashed lines. For clarity, only H atoms involved in intramolecular hydrogen bonding have been included.

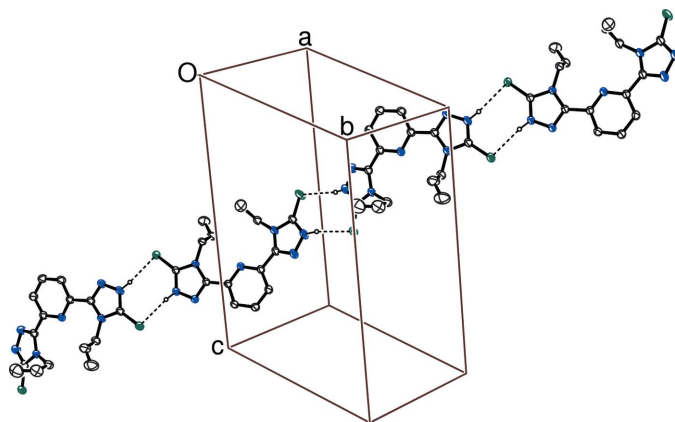


Figure 2

Part of the crystal structure of (II), showing the formation of one-dimensional linear chains of molecules connected by $R_2^2(8)$ rings. Dashed lines show the N—H...S interactions. For the sake of clarity, H atoms not involved in the motif have been omitted.

5.96 (19)° with triazole rings N1–N3/C1/C2 and N5–N7/C11/C12, respectively, while these angles are 21.86 (10) and 14.26 (15)° in molecule *B* for rings N8–N10/C16/C17 and N12–N14/C26/C27, respectively. The rotations of the two triazole rings are mainly due to the steric repulsion between the two allyl groups bonded to the two triazole rings. The C—S bond distances [1.667 (3)–1.676 (3) Å; Table 1] agree well with similar bonds in related compounds, being intermediate between the value of 1.82 Å for a C—S single bond and 1.56 Å for a C=S double bond (McCarrick *et al.*, 1999; Dinçer *et al.*, 2005). The C2—N2, C12—N6, C17—N9 and C27—N13 bond distances of 1.335 (4), 1.335 (4), 1.328 (4) and 1.329 (4) Å, respectively, are indicative of some double-bond character. The C—S and C—N bond lengths mentioned above indicate intermediate character between thione and thiol structures.

In each molecule of (II), two very weak intramolecular hydrogen bonds are observed between the allyl group H and

the pyridine N atoms (Table 2), which lead to the formation of six-membered rings with graph-set descriptor $S(6)$ (Bernstein *et al.*, 1995). In the crystal structure, molecules *A* and *B* are linked alternately by N—H...S hydrogen bonds (Table 2), which form $R_2^2(8)$ rings (Fig. 2). Propagation of these hydrogen-bonded rings generates a chain of molecules running along the $[12\bar{1}]$ direction.

Experimental

Compound (I) was prepared according to our previously reported laboratory method (Çetin, 2004). A stirred mixture of compound (I) (0.393 g, 1 mmol) and sodium hydroxide (40 mg, 1 mmol, as a 2 N aqueous solution) was refluxed for 4 h. After cooling, the solution was acidified with hydrochloric acid and the precipitate was filtered off. The precipitate, (II), was then recrystallized from a mixture of ethanol and dioxane (100 ml, 3:1 v/v) (yield 0.286 g, 80%; m.p. 532 K). IR (ν , cm^{-1}): 3140–3064 (Ar CH), 2980–2878 (Al/Allyl CH), 2945–2762–2560 (SH).

Crystal data

$\text{C}_{15}\text{H}_{15}\text{N}_7\text{S}_2$
 $M_r = 357.46$
 Triclinic, $P\bar{1}$
 $a = 10.0527$ (7) Å
 $b = 10.7295$ (7) Å
 $c = 16.5864$ (12) Å
 $\alpha = 73.027$ (5)°
 $\beta = 88.204$ (6)°
 $\gamma = 89.503$ (6)°

$V = 1710.3$ (2) Å³
 $Z = 4$
 $D_x = 1.388$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.32$ mm⁻¹
 $T = 296$ K
 Prism, colourless
 $0.46 \times 0.35 \times 0.21$ mm

Data collection

Stoe IPDS 2 diffractometer
 ω scans
 Absorption correction: integration
 (*X-RED32*; Stoe & Cie, 2002)
 $T_{\min} = 0.873$, $T_{\max} = 0.940$

25011 measured reflections
 6725 independent reflections
 5075 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\max} = 26.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.147$
 $S = 1.05$
 6725 reflections
 433 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.082P)^2 + 0.6577P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.70$ e Å⁻³
 $\Delta\rho_{\min} = -0.49$ e Å⁻³

Table 1

Selected bond lengths (Å).

S1—C2	1.667 (3)	N7—C12	1.378 (3)
S2—C12	1.671 (3)	N7—C13	1.467 (3)
S3—C17	1.676 (3)	N8—C16	1.307 (4)
S4—C27	1.674 (3)	N8—N9	1.360 (4)
N1—C1	1.305 (4)	N10—C16	1.376 (4)
N1—N2	1.361 (4)	N10—C17	1.376 (4)
N3—C2	1.372 (4)	N10—C18	1.461 (4)
N3—C1	1.373 (4)	N12—C26	1.303 (4)
N3—C3	1.454 (4)	N12—N13	1.366 (4)
N5—C11	1.310 (4)	N14—C27	1.374 (4)
N5—N6	1.360 (3)	N14—C26	1.379 (4)
N7—C11	1.374 (3)	N14—C28	1.478 (4)

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3A···N4	0.97	2.53	3.131 (4)	120
C13—H13A···N4	0.97	2.47	3.054 (4)	118
C18—H18A···N11	0.97	2.47	3.150 (4)	127
C28—H28B···N11	0.97	2.44	3.071 (4)	123
N2—H2···S3 ⁱ	0.86	2.42	3.266 (3)	169
N6—H6···S4 ⁱⁱ	0.86	2.37	3.212 (2)	167
N9—H9A···S1 ⁱ	0.86	2.47	3.297 (3)	163
N13—H13···S2 ⁱⁱ	0.86	2.43	3.288 (3)	172

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x, -y, -z + 2$.

H atoms were positioned geometrically (C—H = 0.93–0.97 Å and N—H = 0.86 Å) and were refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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