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5,5′-Pyridine-2,6-diylbis[4-ethyl-2,4-dihydro-1,2,4-triazole-3(2*H*)-thione]

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.055
wR factor = 0.163
Data-to-parameter ratio = 17.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $C_{13}H_{15}N_7S_2$, the two triazole rings are twisted away from the central pyridine ring by 11.7 (2) and 41.8 (1)°. Inversion-related molecules are linked by N—H···S hydrogen bonds, forming dimers which are linked into a chain by N—H···N hydrogen bonds.

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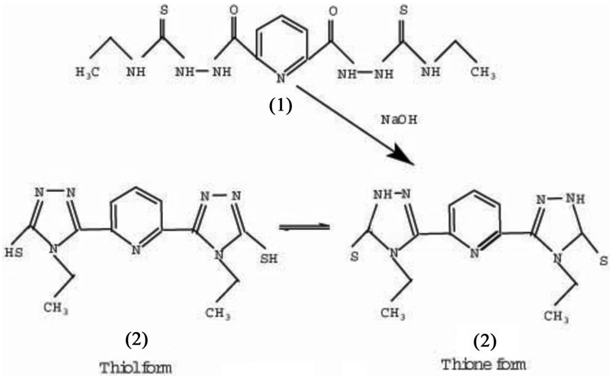
Comment

1,2,4-Triazole and its 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 hypoglycemic properties (Abbas & Khalil, 2005; Koparır *et al.*, 2005; Holla *et al.*, 1998). Carboxylic acid hydrazides are condensed with carbon disulfide in ethanolic potassium hydroxide to yield potassium 3-aroyldithiocarbazates, which are cyclized with hydrazine to the triazole (Cansız *et al.*, 2004; Reid *et al.*, 1976). In addition, there have been some studies of the electronic structures and thiol–thione tautomeric equilibrium of heterocyclic thione derivatives (Koparır *et al.*, 2005; Coyanis *et al.*, 2002). In the present study, 5,5′-pyridine-2,6-diylbis[4-ethyl-2,4-dihydro-1,2,4-triazole-3(2H)-thione], (2), was synthesized by the reaction of ethyl isothiocynate and pyridine-2,6-dicarbohydrazide through 5,5′-pyridine-2,6-diylbis(*N*-ethylhydrazinecarbothioamide), (1). Base-catalysed intramolecular dehydrative cyclization of this intermediate furnished the thione in good yield (85%). The reaction sequence depicted in the scheme was followed to obtain compound (2).



In the title molecule (Fig. 1), the N1–N3/C1/C2 and N5–N7/C10/C11 rings are twisted away from the central pyridine ring by 11.7 (2) and 41.8 (1)°, respectively. Inversion-related molecules are linked by N—H···S hydrogen bonds, forming a dimer. N—H···N hydrogen bonds (Table 1) link the dimers into a chain (Fig. 2).

Experimental

A mixture of 5,5′-pyridine-2,6-diylbis(*N*-ethyllhydrazinecarbothioamide) (0.479 g, 1 mmol) and sodium hydroxide (40 mg, 1 mmol, as a 2*N* solution) was refluxed with stirring for 4 h. After cooling, the solution was acidified with hydrochloric acid and the resulting precipitate was filtered off and then crystallized from a methanol–dioxan (1:1) mixture (yield: 0.28 g, 85%; m.p. 600.7 K). IR (KBr, υ, cm^{-1}): 3160–3010 (aryl CH), 2920–2870 (aliphatic CH), 2940–2756–2560 (SH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 14.16 (*br*, 2H, 2 × SH), 8.10–8.23 (*m*, 3H, aryl CH), 4.42 (*q*, *J* = 6.80, 2 × 2H, N–CH$_2$–CH$_3$), 4.42 (*t*, *J* = 6.82, 2 × 3H, N–CH$_2$–CH$_3$).

Crystal data

$C_{13}H_{15}N_7S_2$
$M_r = 333.46$
Monoclinic, $P2_1/c$
$a = 6.7330$ (6) Å
$b = 18.4906$ (13) Å
$c = 12.3576$ (12) Å
$\beta = 100.162$ (8)°
$V = 1514.4$ (2) Å^3
$Z = 4$
$D_x = 1.463$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.36$ mm^{-1}
$T = 296$ K
Prism, colourless
0.46 × 0.32 × 0.21 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{\min} = 0.875$, $T_{\max} = 0.931$
15631 measured reflections
3574 independent reflections
2126 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.110$
$\theta_{\max} = 28.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.163$
$S = 0.98$
3574 reflections
201 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0925P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.63$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.019 (4)

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N2—H2⋯N6$^{\rm i}$	0.86	2.26	3.051 (3)	154
N7—H7*A*⋯S2$^{\rm ii}$	0.86	2.43	3.278 (2)	169

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

Atoms C12 and C13 of the ethyl group are disordered over two sites, with a site-occupation factor of 0.538 (4) for the major conformation. H atoms were positioned geometrically, with C—H = 0.93–0.97Å and N—H = 0.86Å, and refined using a riding model, with $U_{\rm iso}$(H) = 1.2 (1.5 for methyl) times $U_{\rm eq}$(carrier).

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* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

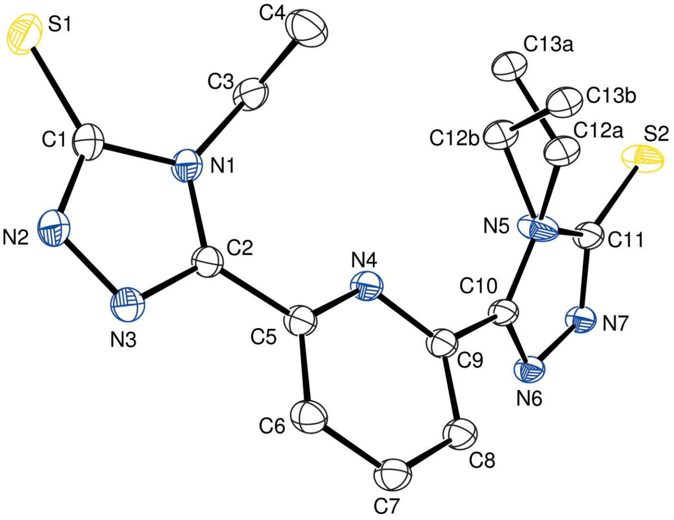


Figure 1
An ORTEP-3 (Farrugia, 1997) drawing of (2), showing the atomic numbering scheme. Displacement ellipsoids of non-H atoms are drawn at the 40% probability level. Both the major and minor components of the disordered ethyl group are shown. H atoms have been omitted.

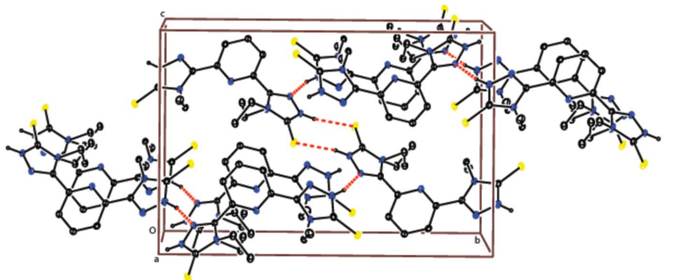


Figure 2
A projection of the crystal structure of (2) approximately along the *a* axis. Dashed lines indicate the N—H⋯N and N—H⋯S interactions. H atoms not involved in hydrogen bonding have been omitted.

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