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4,4′-Dibenzyl-5,5′-(pyridine-2,6-diyl)-bis(3,4-dihydro-2*H*-1,2,4-triazole-3-thione)

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.093
Data-to-parameter ratio = 18.2

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

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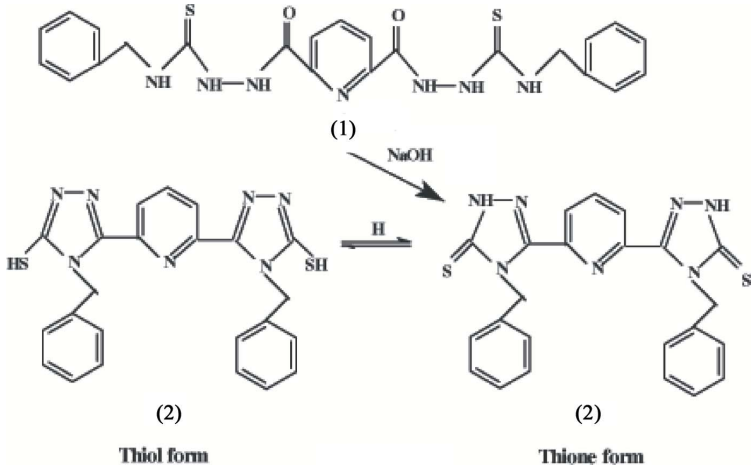
The title compound, $C_{23}H_{19}N_7S_2$, adopts the ketoamine tautomeric form and displays C—H···N hydrogen-bonding interactions. There are two independent molecules in the asymmetric unit.

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, anticonvulstant, antidepressant, antihypertensive, analgaesic and hypoglycaemic properties (Abbas *et al.*, 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 are 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, 4,4′-dibenzyl-5,5′-(pyridine-2,6-diyl)bis(2,4-dihydro-3H-1,2,4-triazole-3-thione), (2), was synthesized by the reaction of benzyl isothiocynate and pyridine-2,6-dicarbohydrazide through 5,5′-pyridine-2,6-diylbis(*N*-phenylhydrazinecarbothioamide), (1). Base-catalysed intramolecular dehydrative cyclization of this intermediate furnished the thione in good yield (80%). The reaction sequence depicted in the scheme was followed to obtain compound (2).



The asymmetric unit of (2) contains two independent molecules. Fig. 1 shows the positions of these two molecules relative to one another. There are two intramolecular C—H···N and C—H···π interactions in the structure of (2) (Table 1). The average value of the C=N double-bond length

in (2) is 1.302 (2)Å, in agreement with those in similar compounds.

Experimental

A mixture of pyridine-2,6-dicarbohydrazide (0.01 mol) and the appropriate benzyl isothiocynate (0.01 mol) in absolute ethanol (100 ml) was refluxed for 8 h. The solid material obtained on cooling was filtered off, washed with diethy ether, dried and crystallized from ethanol (yield 80%; m.p 391–392 K) to give (1). To synthesize compound (2), a mixture of compound (1) (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 mixture of methanol–dioxane (2:1) (yield: 0.37 g, 80%; m.p. 531 K). IR (KBr, ν, cm^{-1}): 3130–3020 (aryl CH), 2950–2910 (aliphatic CH), 2945–2762–2560 (S—H); ^{1}H NMR (400 MHz, DMSO-d_6, δ, p.p.m.): 14.29 (*br*, 2H, 2 × SH), 8.05 (*t*, J = 5.70 Hz, 1H, Pr-CH), 7.90 (*d*, J = 6.00 Hz, 2H, Pr-CH), 7.18–7.30 (*m*, 10H, 2 × Ph-CH), 5.17 (*s*, 4H, 2 × N—CH$_2$—Ph).

Crystal data

$C_{23}H_{19}N_7S_2$
M_r = 457.57
Triclinic, $P\overline{1}$
a = 10.6469 (7) Å
b = 10.8127 (7) Å
c = 21.9501 (13) Å
α = 89.500 (5)°
β = 89.496 (5)°
γ = 61.774 (5)°
V = 2226.3 (2) Å^3
Z = 4
D_x = 1.365 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.27 mm^{-1}
T = 296 K
Prism, colourless
0.62 × 0.48 × 0.26 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.853, T_{max} = 0.934
32857 measured reflections
10510 independent reflections
6295 reflections with $I > 2\sigma(I)$
R_{int} = 0.094
θ_{max} = 28.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.093
S = 0.90
10510 reflections
578 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0353P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C17—H17B···N4	0.97	2.44	3.099 (2)	125
C40—H40A···N11	0.97	2.49	3.054 (2)	117

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_{iso}(H) = 1.2U_{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).

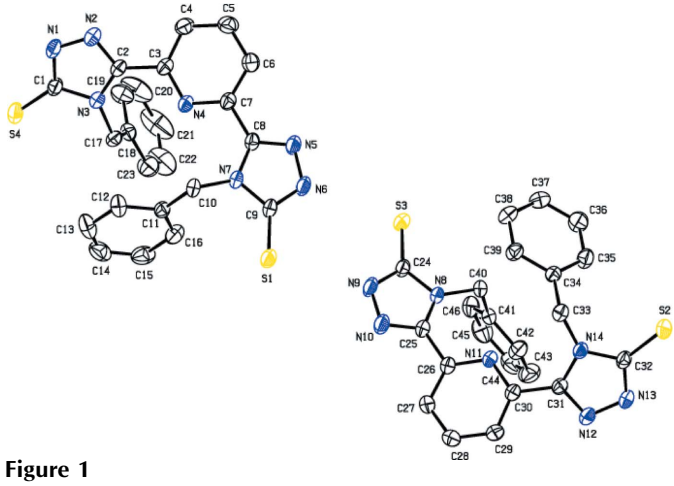


Figure 1
The asymmetric unit of (2), showing the atomic numbering scheme. Displacement ellipsoids of non-H atoms are drawn at the 30% probability level and H atoms have been omitted for clarity.

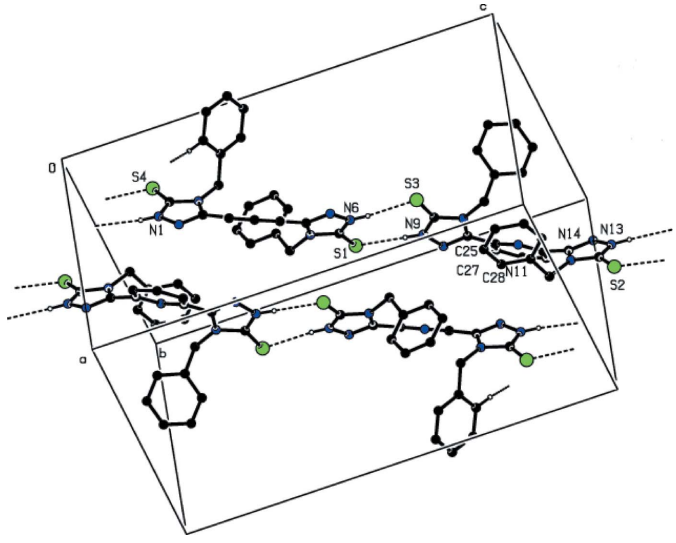


Figure 2
A view of the packing and hydrogen-bonding interactions (dashed lines) of (2). H atoms not involved in hydrogen bonding have been omitted.

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