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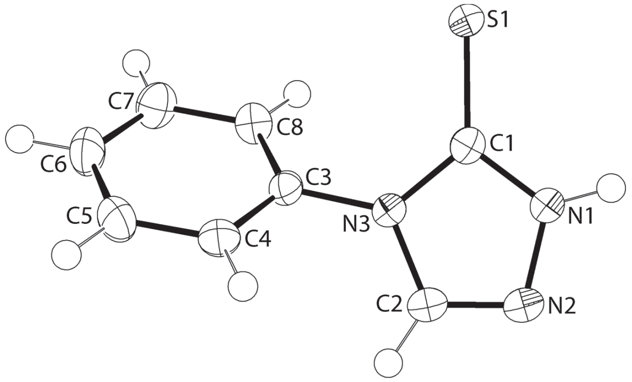
Crystal structure of 4-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione, $C_8H_7N_3S$



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Abstract

$C_8H_7N_3S$, monoclinic, $P2_1/c$ (no. 14), $a = 6.0155(1)$ Å, $b = 14.1062(1)$ Å, $c = 10.1990(1)$ Å, $\beta = 98.871(1)°$, $V = 855.092(18)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0241$, $wR_{ref}(F^2) = 0.0609$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Phenyl isothiocyanate (Merck; 1.19 mL, 0.01 mol) in ethanol (10 mL) was added dropwise to an equimolar amount of formic hydrazide (Merck; 0.60 g, 0.01 mol) in ethanol (10 mL). The resulting mixture was stirred for 2 h and left for evaporation at room temperature, yielding colourless crystals after 2 weeks. **M.pt** (Biobase automatic melting point apparatus MP450, uncorrected): 438.15–439.15 K. **Elem. Anal.** (Leco TruSpec Micro CHN Elemental Analyser): Calc. for $C_8H_7N_3S$: C, 54.22; H, 3.98; N, 23.71%. Found: C, 54.30; H, 4.00; N, 23.75%. **IR** (Bruker Vertex 70v FTIR spectrophotometer from 4000 to 400 cm^{-1}): 3107 (m) ν(N—H), 1485 (vs) ν(C—N), 1281 (vs) ν(C=S). **^{1}H-NMR** (Bruker Ascend 400 MHz; $CDCl_3$): δ [ppm] 12.37 (s, br, 1H, NH), 7.96 (s, 1H, CH), 7.60–7.49 (m, 5H, aryl-H). **^{13}C{^{1}H}-NMR** (Bruker Ascend 400 MHz; $CDCl_3$): δ [ppm] 167.4 (Cq), 140.9 (NCN), 133.7 (Ph, C1), 129.1 (Ph, C2 & 4, overlapped), 125.6 (Ph, C3).

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.25 \times 0.16 \times 0.13$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	2.91 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9519, 1525, 0.018
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1477
$N(param)_{refined}$:	112
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	$U_{iso}*/U_{eq}$
S1	0.26316(5)	0.42759(2)	−0.11406(3)	0.01791(11)
N1	0.17901(19)	0.43745(8)	0.13988(11)	0.0173(2)
H1N	0.069(2)	0.4798(10)	0.1273(16)	0.026*
N2	0.22991(19)	0.39594(8)	0.26285(11)	0.0219(3)
N3	0.42383(18)	0.33163(8)	0.11766(10)	0.0163(2)
C1	0.2907(2)	0.39986(9)	0.04831(13)	0.0153(3)
C2	0.3783(2)	0.33269(10)	0.24575(13)	0.0217(3)
H2	0.447849	0.291655	0.313813	0.026*
C3	0.5751(2)	0.26640(9)	0.06913(12)	0.0165(3)
C4	0.5604(2)	0.17121(10)	0.10172(14)	0.0221(3)
H4	0.449929	0.150148	0.152328	0.027*
C5	0.7098(3)	0.10739(10)	0.05922(15)	0.0267(3)
H5	0.703335	0.042280	0.082143	0.032*
C6	0.8683(2)	0.13818(10)	−0.01653(15)	0.0260(3)
H6	0.968920	0.094062	−0.046267	0.031*
C7	0.8800(2)	0.23342(10)	−0.04893(14)	0.0232(3)
H7	0.988158	0.254157	−0.101366	0.028*
C8	0.7345(2)	0.29868(9)	−0.00521(13)	0.0187(3)
H8	0.744028	0.364092	−0.025813	0.022*

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Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95 Å) and refined as riding with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$. The N-bound H-atom was located in a difference Fourier map but was refined with a distance restraint of N—H = 0.88 ± 0.01 Å, and with $U_{\mathrm{iso}}(\mathrm{H})$ set to $1.2U_{\mathrm{equiv}}(\mathrm{N})$.

Comment

The crystal and molecular structures of the title compound were determined as part of on-going studies into the structural chemistry of 1,2,4-triazole-5-thiones [5], compounds of interest owing to their potential pharmacological [6, 7]; they are also known to coordinate metals [8].

The molecule in the title compound is shown in the figure (70° probability displacement ellipsoids) and features a strictly planar 1,2,4-triazole ring with r.m.s. deviation of the fitted atoms being 0.0057 Å. The appended thione-S1 and ipso-C3 atoms lie 0.084(1) and 0.044(1) Å out of the plane, respectively. The planarity does not extend to the pendant phenyl ring as seen in the dihedral angle of 47.45(7)° between the aforementioned rings. The crystallographic study proves the molecule to exist in the thione form rather than the thiol tautomer as seen in the S1—C1 bond length of 1.6847(13) Å. Within the five-membered ring, the short C2—N2 bond length [1.2927(18) Å] compares with the longer C1—N1 [1.3409(17) Å], C1—N3 [1.3760(16) Å] and C2—N3 [1.3756(17) Å] bond lengths; N1—N2 is 1.3752(16) Å. The N2—N1—C1 angle of 113.69(11)° is wider than the N1—N2—C2 angle of 103.42(10)°, again consistent with protonation at the N1 atom. These observations are as observed for the recently described 4-chlorophenyl derivative [5] as well as for the derivatives with a *N*-bound methyl group [9] and *N*-bound 2-morpholinoethyl substituent [10].

The formation of an eight-membered $\{\cdots\mathrm{HNCS}\}_2$ synthon is the key feature of the molecular packing [N1—H1n$\cdots$S1$^{\mathrm{i}}$: H1n$\cdots$S1$^{\mathrm{i}}$ = 2.374(13) Å, N1$\cdots$S1$^{\mathrm{i}}$ = 3.2485(12) Å with an angle at H1n = 169.3(12)° for symmetry operation i: −x, 1 − y, −z]. The two-molecule aggregates stack in columns along the *a*-axis. Connections between these leading to a three-dimensional architecture are of the type phenyl-C—H$\cdots$N(imine) [C5—H5$\cdots$N2$^{\mathrm{ii}}$: H5$\cdots$N2$^{\mathrm{ii}}$ = 2.59 Å, C5$\cdots$N2$^{\mathrm{ii}}$ = 3.4812(18) Å with angle at H5 = 156° for symmetry operation ii: 1 − x, −1/2 + y, 1/2 − z] and triazolyl-C—H$\cdots\pi$(phenyl) [C2—H2$\cdots$Cg(C3—C8)$^{\mathrm{iii}}$: H2$\cdots$Cg(C3—C8)$^{\mathrm{iii}}$ = 2.51 Å, C2$\cdots$Cg(C3—C8)$^{\mathrm{iii}}$ = 3.2994(14) Å with angle at H2 = 140° for symmetry operation iii: x, 1/2 − y, 1/2 + z].

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