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4-Amino-5-(4-chlorophenoxymethyl)-2-(2-cyanoethyl)-2*H*-1,2,4-triazole-3(4*H*)-thione monohydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.058
wR factor = 0.133
Data-to-parameter ratio = 13.5

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

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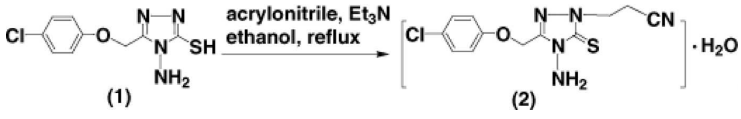
In the title molecule, $C_{12}H_{12}ClN_5OS\cdot H_2O$, all the bond lengths and angles have normal values. O—H···O, O—H···N, N—H···S, C—H···O and C—H···N hydrogen bonds, with C—H···π interactions, link the molecules into a three-dimensional network.

Comment

1,2,4-Triazole (Wang *et al.*, 1997) and related compounds exhibit interesting and useful biological activities (Eisa, 1990). The encouraging biological activities of these heterocycles prompted us to synthesize derivatives which may be suitable targets for antibiotic design. The title compound, (2), was synthesized by Michael reaction of (1) and acrylonitrile in the presence of triethylamine. It has been proved that the acidity of the NH group is stronger than that of the SH group on the ring of the triazole in the Michael reaction (Shi *et al.*, 2004). When the 4-position is substituted by amino, the NH group is still the reaction position of the Michael reaction. The structure of compound (2) was confirmed by X-ray single-crystal diffraction analysis.



All the bond lengths and angles in (2) have normal values. The N1/C9/N2/N3/C8 ring and atom S1 are approximately coplanar; the C8—N1—C9—S1 torsion angle is 176.8 (3)°. The bond length of C9—S1 [1.668 (3) Å] characterizes it as a C=S double bond compared with the literature value for the length of a C—S single bond [1.731 (2) Å; Tripolt *et al.*, 1993] and the length of a C=S double bond connected to a triazole ring [1.669 (2) Å; Seccombe & Kennard, 1973]. This suggests extensive conjugation of the C=S bond with the triazole ring.

In the crystal structure of (2), the molecules are linked *via* O—H···O, O—H···N, N—H···S, C—H···O and C—H···N hydrogen bonds (Table 1) involving the solvent water molecules and amino groups to form a three-dimensional network. In addition, C—H···π interactions involving C7/H7*B* and the C1–C6 benzene ring (centroid *Cg*) are observed.

Experimental

To a well stirred solution of 4-amino-3-*p*-chlorophenyloxymethyl-5-mercapto-1,2,4-triazole, (1) (2.5 mmol), anhydrous ethanol (5 ml) and triethylamine (3 mmol) was added acrylonitrile (3 mmol), and the resulting solution was refluxed for 90 min (monitored by thin-layer chromatography). At the end of the reaction, the mixture was cooled to room temperature and neutralized, and the solvent was

removed *in vacuo*. The crude product was purified by column chromatography (silica gel, 20 g; petroleum ether–trichloromethane–ethanol 5:2:0.5) to give compound (2) as white crystals. Colourless single crystals of (2) suitable for X-ray crystallographic analysis were obtained by recrystallization from ethyl acetate. ^{1}H NMR (300 MHz, $CDCl_3$, δ, p.p.m.): 7.31–7.28 (*d*, H2, H4), 6.96–6.93 (*d*, H1, H5), 5.12 (*s*, H7*A*,H7*B*), 4.82 (*s*, *br*, H4*A*, H4*B*), 4.52–4.47 (*t*, H10*A*, H10*B*), 3.00–2.96 (*t*, H11*A*, H11*B*); ^{13}C NMR (300 MHz, $CDCl_3$, δ, p.p.m.): 167.4, 155.0, 147.2, 129.6, 127.2, 116.4, 116.2, 59.5, 45.0, 16.5.

Crystal data

$C_{12}H_{12}ClN_5OS\cdot H_2O$
M_r = 327.79
Triclinic, $P\overline{1}$
a = 7.330 (18) Å
b = 8.944 (11) Å
c = 11.734 (17) Å
α = 90760 (11)°
β = 94210 (16)°
γ = 99.01 (14)°
V = 757.5 (2) Å^3
Z = 2
D_x = 1.437 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.40 mm^{-1}
T = 293 (2) K
Prism, colourless
0.30 × 0.30 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.889, T_{max} = 0.906
3406 measured reflections
2717 independent reflections
2231 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 25.2°
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.133
S = 1.06
2717 reflections
202 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 0.99P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

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

Cg is the centroid of the benzene ring.

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2*A*···O2^{i}	0.85 (5)	2.52 (5)	3.046 (7)	121 (4)
O2—H2*B*···N5^{ii}	0.83 (5)	2.54 (5)	3.338 (5)	162 (5)
N4—H4*A*···S1^{iii}	0.84 (4)	2.66 (4)	3.499 (4)	174 (4)
N4—H4*B*···S1	0.82 (4)	2.83 (4)	3.239 (3)	113 (3)
C10—H10*A*···O2^{iv}	0.97	2.47	3.421 (5)	167
C11—H11*B*···N4^{v}	0.97	2.59	3.550 (5)	172
C7—H7*B*···*Cg*^{vi}	0.97	2.70	3.486 (4)	139

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

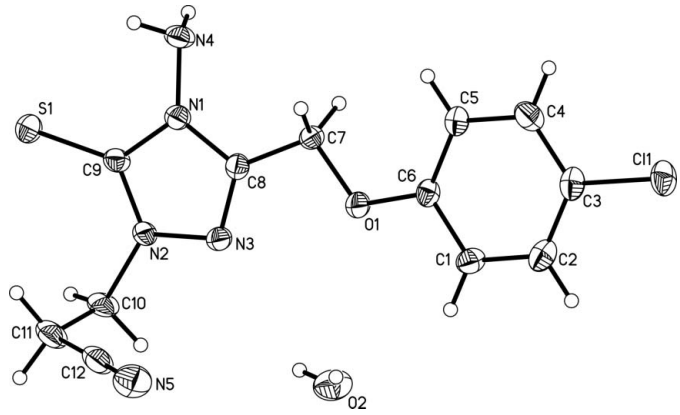


Figure 1
The molecular structure of (2), with 30% probability displacement ellipsoids.

The water and amine H atoms were located in a difference map and they were refined with U_{iso}(H) = 1.2U_{eq}(O,N). C-bound H atoms were positioned geometrically (C—H = 0.93 or 0.97 Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(parent atom).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXL97*.

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