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Crystal structure of 2-(2-(1-Chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl)-1*H*-1,2,4-triazole-3(2*H*)-thione, C₁₄H₁₅Cl₂N₃OS

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.16 × 0.16 × 0.14 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	5.5 cm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{\max}$, completeness:	51°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11684, 2936, 0.017
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2656
$N(\text{param})_{\text{refined}}$:	196
Programs:	Bruker programs [1], SHELX [2]

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Abstract

C₁₄H₁₄Cl₂N₃OS, monoclinic, $P2_1/n$ (no. 14), $a = 9.9215(8)$ Å, $b = 9.5992(7)$ Å, $c = 16.5801(13)$ Å, $\beta = 92.702(1)^\circ$, $V = 1577.3(2)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0323$, $wR_{\text{ref}}(F^2) = 0.0918$, $T = 296$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Source of material

The synthesis process of prothioconazole is carried out using 2-(1-chlorocyclopropyl)-1-(2-chlorophenyl)-3-hydrazinylpropan-2-ol as starting material, and reacting in the first step with paraformaldehyde and ammonium thiocyanate and allowing the resulting product to react in the second step with oxygen in the presence of potassium hydroxide and sulphur powder. 2-(1-chlorocyclopropyl)-1-(2-chlorophenyl)-3-(2,5-dihydro-1*H*-1,2,4-triazol-1-yl) propan-2-ol (5 mol, 1.72 g), sulphur (0.01 mg) and potassium hydroxide powder (6 mol, 0.34 g) was dissolved in 20 mL absolute toluene. The mixture was heated at 70 °C for 12 h. The progress of the reaction is monitored by TLC analysis. After cooling to room temperature, the reaction mixture is diluted with methyl tert-butyl ether and extracted with saturated aqueous ammonium chloride solution (325 mL). The organic phase is dried over MgSO₄, filtered and concentrated under reduced pressure. This obtain 2.2 g of a crude product, and then recrystallize from toluene to give 1.4 g white solid 2-(2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl)-1,2-dihydro-3*H*-1,2,4-triazole-3-thione. m.p: 137–139 °C. Analysis calculated for C₁₄H₁₅Cl₂N₃OS: C, 48.85; H, 4.39; N, 12.21%; found: C, 49.01; H, 4.66; N, 12.47%.

Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with C–H = 0.96–0.97 Å with

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.7323(2)	0.66482(17)	0.61436(10)	0.0516(4)
H1	0.6794	0.7376	0.5935	0.062*
C2	0.84031(14)	0.53053(14)	0.70284(9)	0.0321(3)
C3	0.92735(15)	0.36509(15)	0.60076(9)	0.0361(3)
H3A	0.9895	0.3362	0.6445	0.043*
H3B	0.9804	0.3911	0.5554	0.043*
C4	0.83687(15)	0.24171(15)	0.57598(8)	0.0329(3)
C5	0.92447(16)	0.11124(15)	0.56248(9)	0.0381(3)
H5A	0.8649	0.0354	0.5457	0.046*
H5B	0.9821	0.1305	0.5181	0.046*
C6	1.01250(15)	0.06181(15)	0.63334(9)	0.0347(3)
C7	0.96042(17)	−0.02691(17)	0.69042(11)	0.0457(4)
H7	0.8705	−0.0539	0.6842	0.055*
C8	1.0371(2)	−0.0763(2)	0.75583(12)	0.0591(5)
H8	0.9989	−0.1356	0.7928	0.071*
C9	1.1700(2)	−0.0377(2)	0.76620(12)	0.0640(5)
H9	1.2217	−0.0693	0.8107	0.077*
C10	1.22629(19)	0.0479(2)	0.71047(12)	0.0563(5)
H10	1.3165	0.0738	0.7169	0.068*
C11	1.14863(15)	0.09504(16)	0.64506(9)	0.0397(3)
C12	0.75051(17)	0.26781(17)	0.49824(10)	0.0431(4)
C13	0.61365(19)	0.3310(2)	0.49738(13)	0.0613(5)
H13A	0.5885	0.3944	0.4537	0.074*
H13B	0.5769	0.3541	0.5489	0.074*
C14	0.6296(2)	0.1794(2)	0.47708(13)	0.0633(5)
H14A	0.6028	0.1113	0.5164	0.076*
H14B	0.6144	0.1517	0.4211	0.076*
Cl1	1.22774(5)	0.19811(5)	0.57459(3)	0.05949(15)
Cl2	0.84950(6)	0.31206(6)	0.41537(3)	0.06604(17)
N1	0.76161(14)	0.64550(13)	0.69401(8)	0.0401(3)
N2	0.78618(17)	0.57066(14)	0.57046(8)	0.0518(4)
N3	0.85275(13)	0.48627(12)	0.62649(7)	0.0365(3)
O1	0.75012(11)	0.22343(11)	0.64115(6)	0.0385(2)
H1A	0.7121	0.1478	0.6367	0.058*
S1	0.90906(4)	0.46187(4)	0.78907(2)	0.03918(12)
H2	0.7362(18)	0.6930(19)	0.7305(11)	0.043(5)*

$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2 U_{\text{eq}}(\text{C})$ for all other H atoms.

Discussion

Prothioconazole, [2-(2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl)-1,2-dihydro-3H-1,2,4-triazole-3-thione], was a new generation triazolinthione fungicide developed by Bayer Company and appeared on the market in 2004 [3, 4]. Prothioconazole is a systemic fungicide with protective, curative, and eradivative activities, which inhibits ergosterol biosynthesis by directly binding to CYP51 (sterol 14a-demethylase), therefore resulting in the depletion of ergosterol and the concomitant increase in 14a-methylated sterols [5–7]. This fungicide has been widely used to control

powdery mildew, Fusarium head blight, rusts, and sclerotium on corn, legume crops, and other economic crops [8]. Because of its wild fungicidal activity and its wild applications, the synthesis and biological activity of prothioconazole and its intermediates have attracted much attention [9–12].

The molecular structure of the title compound is shown in the figure, the dihedral angles between the triazole ring, the C1–C6 chloro-phenyl ring and the cyclopropane moiety are 79.5°, 73.2° and 70.0°. In the crystal, an intermolecular O–H···S hydrogen bond link the molecules into one-dimensional chains.

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