5-[1-(3,4-Dichlorophenoxy)ethyl]-1,3,4-oxadiazole-2(3H)-thione hemihydrate

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In the title compound, $C_{10}H_8Cl_2N_2O_2S \cdot 0.5H_2O$, the atoms in the oxadiazole ring are essentially coplanar (r.m.s. deviation 0.010 Å). The crystal structure is stabilized by intermolecular N—H⋯O hydrogen bonds involving the water molecule, which is situated on an a twofold rotation axis, and two organic molecules, leading to a thione tautomer in the solid state. The C atom attached to the oxadiazole ring adopts a typical sp^3 hybridization. The dihedral angle between the mean plane of the benzene ring of the dichlorophenyl group and the mean plane of the oxadiazole ring is 74.18 (4)°. The crystal structure is stabilized by intermolecular N—H⋯O and O—H⋯S hydrogen bonds.

Related literature

For the structures and properties of oxadiazoles, see: Almasirad *et al.*, (2004); Aboraia *et al.* (2006); Akhtar, Hameed, Al-Masoudi *et al.* (2008); Khan *et al.* (2005); Akhtar, Hameed *et al.* (2007); Akhtar, Hameed, Khan *et al.* (2008); Akhtar, Rauf *et al.* (2007); Aydogan *et al.*, 2002). For a related structure, see: Thamotharan *et al.* (2005). For bond-length data, see: Allen *et al.* (1987).
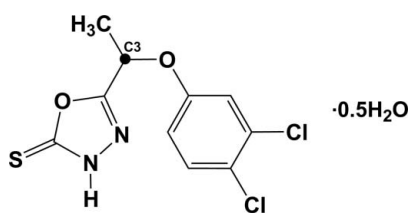
Experimental

Crystal data

$C_{10}H_8Cl_2N_2O_2S \cdot 0.5H_2O$	$V = 2490.38$ (6) Å^3
$M_r = 300.15$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 11.8725$ (2) Å	$\mu = 0.68$ mm^{-1}
$b = 7.89510$ (10) Å	$T = 123$ K
$c = 26.6092$ (4) Å	$0.40 \times 0.30 \times 0.25$ mm
$\beta = 92.9130$ (10)°	

Data collection

Bruker SMART CCD area-detector diffractometer	3088 independent reflections
	2490 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{int} = 0.019$
10568 measured reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.078$	
$S = 1.09$	
3088 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
162 parameters	$\Delta\rho_{min} = -0.21$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O1W	0.86	2.06	2.9084 (16)	168
O1W—H1W⋯S1[i]	0.846 (17)	2.612 (18)	3.3854 (13)	152.5 (17)

Symmetry code: (i) $x + \frac{1}{2}, y + \frac{1}{2}, z$.

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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supporting information

5-[1-(3,4-Dichlorophenoxy)ethyl]-1,3,4-oxadiazole-2(*3H*)-thione hemihydrate

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S1. Comment

1,3,4-Oxadiazoles are an important class of five-membered heterocycles. They show diverse biological activities, for example, antifungal, antibacterial (Almasirad *et al.*, 2004), anti-convulsant (Aboraia *et al.* 2006), antitumour (Akhtar, Hameed, Khan *et al.*, 2008) and enzyme inhibitory activities (Khan *et al.*, 2005). In continuation to our work on five membered heterocycles (Akhtar & Hameed *et al.*, 2007), the title compound was synthesized and evaluated for its biological activities (Akhtar *et al.*, 2008*a*). Herein, we report on the crystal structure of 5-[1-(3,4-dichlorophenoxy) ethyl]-1,3,4-oxadiazole-2(*3H*)-thione, derived from 3,4-dichlorophenoxy propionic acid (Akhtar & Rauf *et al.*, 2007).

The molecular structure of the title compound is illustrated in Fig. 1. The dihedral angle between the mean planes of the benzene and 1,3,4-oxadiazole rings is 74.18 (4)°. The bond lengths and angles are in good agreement with the expected values (Allen *et al.*, 1987; Thamotharan *et al.*, 2005). The N1—N2 [1.3817 (16) A°] and C1=S1 [1.6489 (13) A°] bond lengths correspond to the usual single bond N—N distance and C=S distance.

1,3,4-Oxadizole-2-thiones/thiols can exist in two tautomeric forms (Aydogan *et al.*, 2002). In the title compound the thione form is observed. The H-atom of the thiol group has been transferred to the adjacent N atom of the oxadiazole ring (Fig. 1).

The title compound crystallized as a hemihydrate, with the water molecule lieing on a crystallographic two-fold axis. The water molecule O-atom hydrogen bonds to the NH group, while the water H-atom hydrogen bonds to the S-atom of the *S*=C moiety (see Table 1 and Fig. 2).

S2. Experimental

3,4-dichlorophenoxy acid hydrazide (10.30 mmol) was stirred with KOH (12.37 mmol) dissolved in methanol (30 ml). Carbon disulfide (0.75 mL, 12.37 mmol) was added slowly with stirring. The yellow solution obtained was refluxed until the evolution of hydrogen sulfide had ceased (18h). The reaction mixture was then cooled to rt and filtered. The filtrate was then poured into ice cooled water and acidified with 6M HCl until the colour turned congo red. The precipitate that formed was filtered off and dried. Recrystallization from ethanol/water (1:1) afforded colorless block-like crystals, suitable for X-ray diffraction analysis.

S3. Refinement

The water H-atom was located from a difference electron-density map and refined (O-H = 0.846 (17) Å), with $U_{iso}(H) = 1.3U_{eq}(O)$. The other H-atoms were placed in idealized positions and treated as riding atoms: N-H = 0.86 Å, C—H = 0.93 - 0.98 Å with $U_{iso}(H) = 1.2U_{eq}(N,C)$ or $1.5U_{eq}(C_{methyl})$.
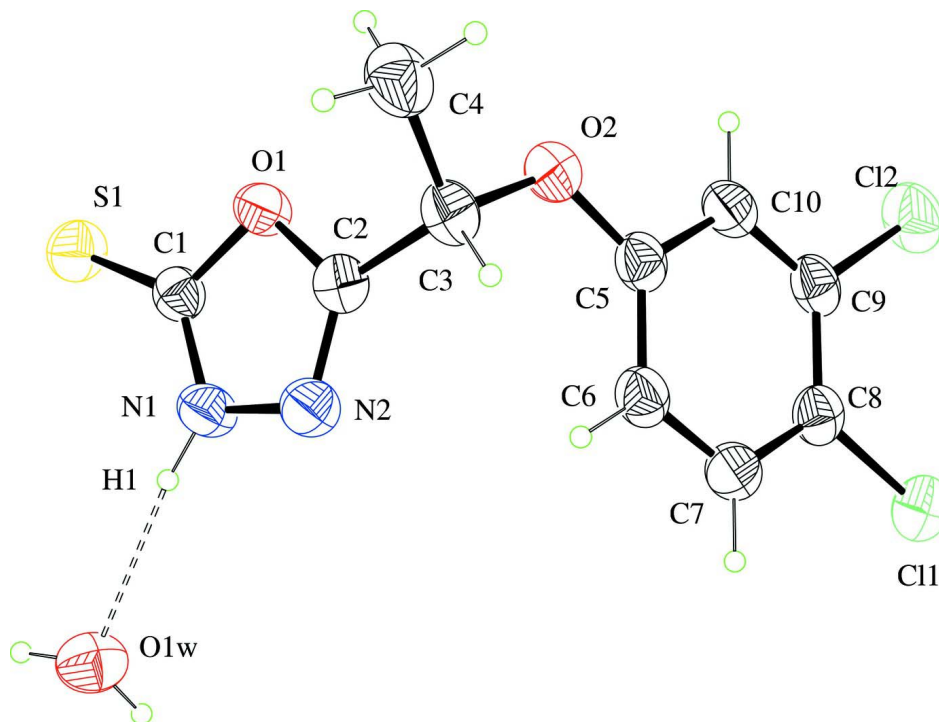
Figure 1

Molecular structure of the title compound, showing the atom-labelling scheme and displacement ellipsoids drawn at the 50% probability level.
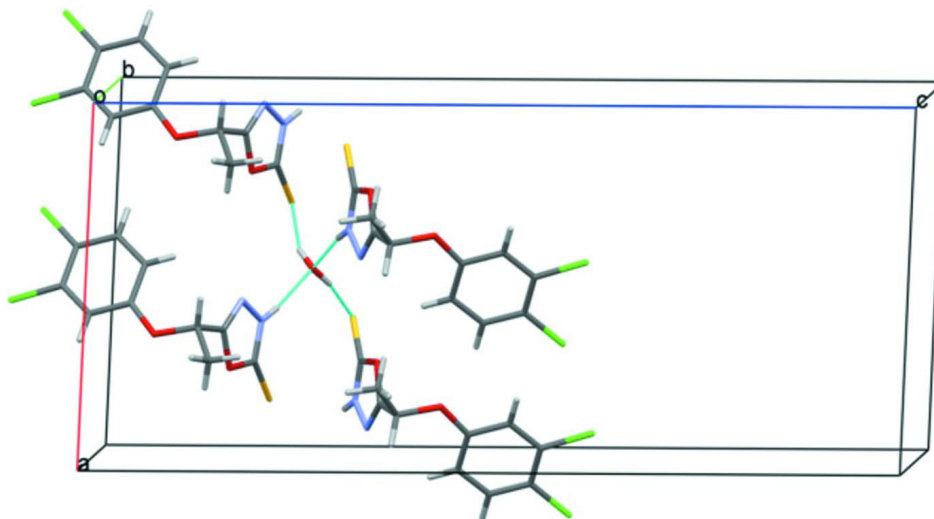
Figure 2

Partial crystal packing diagram of the title compound, viewed along the *a* axis. Hydrogen bonds are shown as dashed pale-blue lines.

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Crystal data

$C_{10}H_8Cl_2N_2O_2S\cdot0.5H_2O$	$F(000) = 1224$
$M_r = 300.15$	$D_x = 1.601$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 4427 reflections
$a = 11.8725$ (2) Å	$\theta = 3.1–28.3°$
$b = 7.8932$ (1) Å	$\mu = 0.68$ mm^{-1}
$c = 26.6092$ (4) Å	$T = 123$ K
$\beta = 92.913$ (1)°	Block, colorless
$V = 2490.38$ (6) Å^3	$0.40 \times 0.30 \times 0.25$ mm
$Z = 8$	

Data collection

Bruker SMART CCD area-detector diffractometer	2490 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.019$
Graphite monochromator	$\theta_{max} = 28.3°$, $\theta_{min} = 3.1°$
φ and ω scans	$h = -15\rightarrow15$
10568 measured reflections	$k = -10\rightarrow10$
3088 independent reflections	$l = -35\rightarrow35$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.027$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.078$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.09$	
3088 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0399P)^2 + 0.7008P]$
162 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.22$ e Å^{-3}
	$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
O1	0.25873 (7)	0.32348 (12)	0.33123 (4)	0.0347 (2)
C1	0.26630 (11)	0.47444 (17)	0.30643 (5)	0.0321 (3)
S1	0.15653 (3)	0.59419 (5)	0.290316 (15)	0.04313 (11)
N1	0.37606 (9)	0.49544 (15)	0.30057 (4)	0.0373 (3)

H1	0.4040	0.5814	0.2857	0.045*
N2	0.44029 (9)	0.36407 (16)	0.32095 (5)	0.0379 (3)
C2	0.36727 (11)	0.26539 (17)	0.33892 (5)	0.0330 (3)
C3	0.38524 (12)	0.09920 (18)	0.36521 (5)	0.0381 (3)
H3	0.4630	0.0612	0.3616	0.046*
C4	0.30442 (15)	−0.0347 (2)	0.34486 (6)	0.0495 (4)
H4A	0.3187	−0.1393	0.3625	0.074*
H4B	0.3148	−0.0510	0.3096	0.074*
H4C	0.2284	0.0010	0.3495	0.074*
O2	0.36403 (8)	0.11531 (14)	0.41765 (4)	0.0417 (2)
C5	0.44340 (11)	0.18810 (17)	0.45029 (5)	0.0351 (3)
C6	0.54468 (11)	0.25923 (18)	0.43709 (5)	0.0374 (3)
H6	0.5649	0.2584	0.4038	0.045*
C7	0.61526 (11)	0.33147 (19)	0.47429 (5)	0.0379 (3)
H7	0.6830	0.3797	0.4656	0.046*
C8	0.58683 (11)	0.33307 (17)	0.52386 (5)	0.0354 (3)
Cl1	0.67766 (3)	0.42681 (5)	0.568937 (14)	0.04480 (11)
C9	0.48523 (12)	0.26045 (17)	0.53664 (5)	0.0360 (3)
Cl2	0.44427 (3)	0.26092 (6)	0.598122 (14)	0.05328 (13)
C10	0.41405 (11)	0.18835 (18)	0.50013 (5)	0.0380 (3)
H10	0.3464	0.1399	0.5089	0.046*
O1W	0.5000	0.75760 (19)	0.2500	0.0457 (4)
H1W	0.5445 (15)	0.817 (2)	0.2687 (7)	0.059*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0320 (4)	0.0336 (5)	0.0389 (5)	0.0003 (4)	0.0056 (4)	0.0056 (4)
C1	0.0360 (6)	0.0313 (7)	0.0291 (6)	0.0000 (5)	0.0026 (5)	−0.0009 (5)
S1	0.03808 (18)	0.0406 (2)	0.0504 (2)	0.00707 (14)	−0.00080 (15)	0.00403 (16)
N1	0.0354 (5)	0.0342 (6)	0.0425 (6)	0.0001 (5)	0.0062 (5)	0.0078 (5)
N2	0.0337 (5)	0.0384 (6)	0.0419 (6)	0.0037 (5)	0.0046 (5)	0.0045 (5)
C2	0.0349 (6)	0.0327 (7)	0.0315 (6)	0.0034 (5)	0.0032 (5)	−0.0013 (5)
C3	0.0434 (7)	0.0358 (7)	0.0355 (7)	0.0051 (6)	0.0045 (6)	0.0038 (6)
C4	0.0664 (10)	0.0345 (8)	0.0473 (9)	−0.0019 (7)	−0.0005 (7)	0.0028 (7)
O2	0.0414 (5)	0.0494 (6)	0.0344 (5)	−0.0037 (4)	0.0027 (4)	0.0062 (4)
C5	0.0356 (6)	0.0341 (7)	0.0356 (7)	0.0075 (5)	0.0025 (5)	0.0065 (6)
C6	0.0361 (7)	0.0437 (8)	0.0328 (7)	0.0066 (6)	0.0058 (5)	0.0059 (6)
C7	0.0335 (6)	0.0409 (8)	0.0400 (7)	0.0065 (6)	0.0065 (5)	0.0052 (6)
C8	0.0361 (6)	0.0332 (7)	0.0371 (7)	0.0098 (5)	0.0019 (5)	0.0023 (6)
Cl1	0.04519 (19)	0.0466 (2)	0.0423 (2)	0.00724 (15)	−0.00057 (14)	−0.00463 (16)
C9	0.0402 (7)	0.0363 (7)	0.0321 (7)	0.0119 (6)	0.0074 (5)	0.0071 (6)
Cl2	0.0564 (2)	0.0696 (3)	0.03508 (19)	0.00834 (19)	0.01402 (16)	0.00641 (18)
C10	0.0364 (7)	0.0380 (8)	0.0401 (7)	0.0051 (6)	0.0078 (6)	0.0096 (6)
O1W	0.0431 (8)	0.0329 (8)	0.0612 (10)	0.000	0.0048 (7)	0.000

Geometric parameters (Å, º)

O1—C1	1.3672 (16)	O2—C5	1.3745 (17)
O1—C2	1.3733 (15)	C5—C10	1.3882 (19)
C1—N1	1.3306 (16)	C5—C6	1.3884 (19)
C1—S1	1.6489 (13)	C6—C7	1.387 (2)
N1—N2	1.3817 (16)	C6—H6	0.9300
N1—H1	0.8600	C7—C8	1.3783 (19)
N2—C2	1.2763 (18)	C7—H7	0.9300
C2—C3	1.4967 (19)	C8—C9	1.3931 (19)
C3—O2	1.4363 (17)	C8—Cl1	1.7371 (15)
C3—C4	1.509 (2)	C9—C10	1.378 (2)
C3—H3	0.9800	C9—Cl2	1.7302 (14)
C4—H4A	0.9600	C10—H10	0.9300
C4—H4B	0.9600	O1W—H1W	0.846 (17)
C4—H4C	0.9600		
C1—O1—C2	106.18 (10)	H4A—C4—H4C	109.5
N1—C1—O1	104.71 (11)	H4B—C4—H4C	109.5
N1—C1—S1	131.59 (11)	C5—O2—C3	120.17 (10)
O1—C1—S1	123.69 (9)	O2—C5—C10	114.02 (12)
C1—N1—N2	112.63 (11)	O2—C5—C6	125.73 (12)
C1—N1—H1	123.7	C10—C5—C6	120.25 (14)
N2—N1—H1	123.7	C7—C6—C5	119.04 (13)
C2—N2—N1	103.48 (10)	C7—C6—H6	120.5
N2—C2—O1	112.99 (12)	C5—C6—H6	120.5
N2—C2—C3	128.79 (12)	C8—C7—C6	121.23 (13)
O1—C2—C3	118.20 (11)	C8—C7—H7	119.4
O2—C3—C2	110.40 (11)	C6—C7—H7	119.4
O2—C3—C4	105.72 (12)	C7—C8—C9	119.15 (13)
C2—C3—C4	111.92 (12)	C7—C8—Cl1	119.41 (11)
O2—C3—H3	109.6	C9—C8—Cl1	121.44 (10)
C2—C3—H3	109.6	C10—C9—C8	120.36 (12)
C4—C3—H3	109.6	C10—C9—Cl2	118.41 (11)
C3—C4—H4A	109.5	C8—C9—Cl2	121.22 (11)
C3—C4—H4B	109.5	C9—C10—C5	119.97 (13)
H4A—C4—H4B	109.5	C9—C10—H10	120.0
C3—C4—H4C	109.5	C5—C10—H10	120.0

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1*W*	0.86	2.06	2.9084 (16)	168
O1*W*—H1*W*···S1[i]	0.846 (17)	2.612 (18)	3.3854 (13)	152.5 (17)

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