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5-(3-Hydroxyphenyl)-1,3,4-oxadiazole-2(3*H*)-thione hemihydrate

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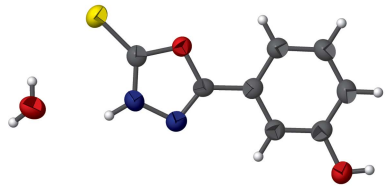
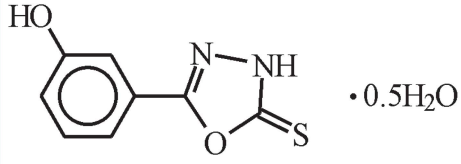
The title 1,3,4-oxadiazole derivative crystallizes as a hemihydrate, $C_8H_6N_2O_2S\cdot 0.5H_2O$, with the water molecule located on a twofold rotation axis. The 1,3,4-oxadiazole molecule is essentially planar, the r.m.s. deviation of the non-H atoms being 0.0443 Å. The dihedral angle between the mean planes of the phenyl and oxadiazole rings is 6.101 (17)°. In the crystal, molecules are linked *via* O—H···S and N—H···O hydrogen bonds involving the water molecule, the N—H group and the thione S atom into undulating ribbons. Additional π–π interactions generate a two-dimensional supramolecular framework extending parallel to (001).

3D view



Chemical scheme



Structure description

Oxadiazoles are an important class of heterocyclic compounds because of their broad biological activities. In particular, 1,3,4-Oxadiazole derivatives are known to act as antibacterial (Ahmed *et al.*, 2018), antimicrobial (Zheng *et al.*, 2018), anticancer (Glomb *et al.*, 2018), anti-inflammatory (Abd-Ellah *et al.*, 2017), analgesic (Husain & Ajmal, 2009), antitubercular (Ali & Shaharyar, 2007; Zampieri *et al.*, 2009), and vasodilatory (Shirote & Bhatia, 2010) agents. They are also important as starting materials for cycloaddition reactions (Vasilev *et al.*, 2007), and are employed in the synthesis of furans (Wolkenberg & Boger, 2002), natural products (Yuan *et al.*, 2005) and plant-growth hormones (Won *et al.*, 2011). Several methods have been reported for the synthesis of 1,3,4-oxadiazoles, the commonly used synthetic routes including reactions of acid hydrazides with acid chlorides/carboxylic acids and direct cyclization of diacylhydrazines

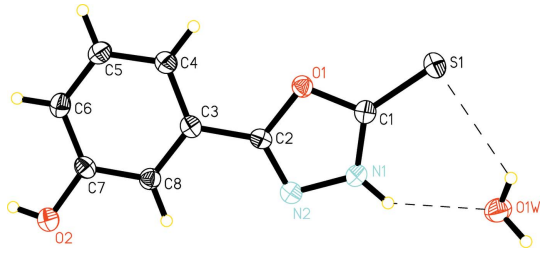


Figure 1
Structures of the molecular entities of the title compound. Displacement ellipsoids are drawn at the 30% probability level; hydrogen bonds are indicated by dashed lines.

using a variety of dehydrating agents such as phosphorous oxychloride (Kadi *et al.*, 2007), thionyl chloride (Mickevičius *et al.*, 2009), or direct reaction of the acid with triphenylphosphorane (Ramazani *et al.*, 2011,2013).

The title 1,3,4-oxadiazole is derived from the condensation of 3-hydroxybenzoic acid hydrazide with potassium butyl xanthate and crystallizes as a hemihydrate (Fig. 1), with the water molecule situated on a twofold rotation axis. The dihedral angle between the mean planes of the phenyl (C3–C8, centroid *Cg*2) and oxadiazole (C1/O1/C2/N2/N, centroid1 *Cg*1) rings is 6.101 (17)°.

In the crystal, the organic molecules are linked into dimers by pairs of N—H···O hydrogen bonds (Table 1), with the O atom of the hydroxy group as the acceptor. Simultaneously, the hydroxy group is also the donor group of a weak hydrogen bond to the S atom of a neighbouring molecule. The water molecule is likewise involved in hydrogen bonding both as a donor and an acceptor, with the S atom and the N—H group as the corresponding acceptor and donor groups, respectively (Table 1). The above-mentioned hydrogen bonds give rise to $R_2^2(16)$ and $R_2^2(6)$ graph-set motifs (Fig. 2), and eventually lead to the formation of undulating ribbons (Fig. 3). Additional π–π stacking between the phenyl and oxadiazole rings [*Cg*1···*Cg*2 (x, 1 + y, z) = 3.6283 (16) Å, slippage = 1.684 Å] consolidates a two-dimensional supramolecular framework extending parallel (001).

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1*W*	0.86	2.26	2.995 (3)	143
N1—H1···O2^{i}	0.86	2.42	3.064 (3)	133
O1*W*—H1*W*···S1	0.85 (4)	2.72 (4)	3.2814 (9)	125 (3)
O2—H2···S1^{ii}	0.82	2.51	3.319 (2)	168

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-\frac{1}{2}, -y+1, z$.

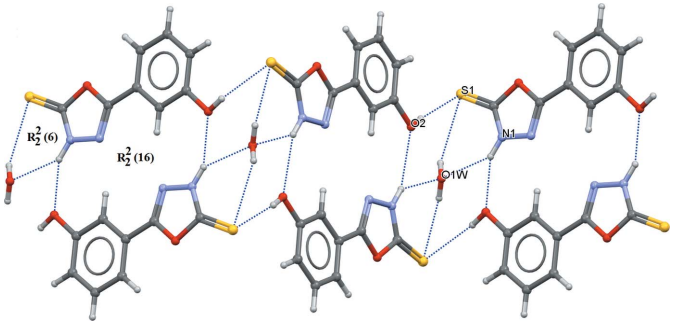


Figure 2
Formation of N—H···O and O—H···S hydrogen bonds (dashed lines) in the crystal structure, leading to $R_2^2(16)$ and $R_2^2(6)$ graph-set motifs.

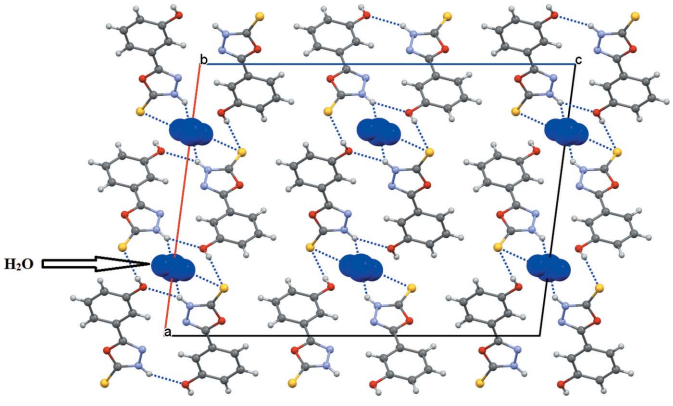


Figure 3
Packing of the molecular entities in the crystal structure, in a view along the *b* axis. Hydrogen bonds are shown as dashed lines.

Synthesis and crystallization

A mixture of 50 mmol of 3-hydroxybenzoic acid hydrazide and 50 mmol of potassium butyl xanthate was dissolved in 100 ml of ethanol and boiled for 8 h. The solvent was distilled off, the residue was diluted with water and acidified with hydrochloric acid to pH = 5–6 (Fig. 4). The resulting mass was filtered, washed with water, dried in air and recrystallized from aqueous ethanol. Small needle-shaped crystals the colour of pale milk were obtained; m.p. 477–478 K.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

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References

Abd-Ellah, H. S., Abdel-Aziz, M., Shoman, M. E., Beshr, E. A. M., Kaoud, T. S. & Ahmed, A. F. F. (2017). *Bioorg. Chem.* **74**, 15–29.
Ahmed, M. N., Sadiq, B., Al-Masoudi, N. A., Yasin, K. A., Hameed, S., Mahmood, T., Ayub, K. & Tahir, M. N. (2018). *J. Mol. Struct.* **1155**, 403–413.

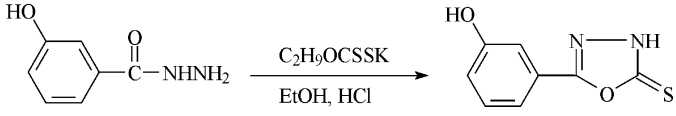

Figure 4
Synthetic scheme for the preparation of the title compound.

Table 2
Experimental details.

Crystal data	
Chemical formula	$2C_8H_6N_2O_2S{\cdot}H_2O$
M_r	406.43
Crystal system, space group	Monoclinic, *I*2/*a*
Temperature (K)	293
a, *b*, *c* (Å)	16.3881 (12), 4.6912 (3), 22.4928 (18)
β (°)	97.512 (7)
V (Å^3)	1714.4 (2)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	3.17
Crystal size (mm)	0.4 × 0.28 × 0.2
Data collection	
Diffractometer	Rigaku Xcalibur Ruby
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.953, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5850, 1767, 1256
R_{int}	0.061
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.629
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.117, 1.04
No. of reflections	1767
No. of parameters	128
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.23

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

Ali, M. A. & Shaharyar, M. (2007). *Bioorg. Med. Chem. Lett.* **17**, 3314–3316.
Glomb, T., Szymankiewicz, K. & Świątek, P. (2018). *Molecules*, **23**, 3361–3377.
Husain, A. & Ajmal, M. (2009). *Acta Pharm.* **59**, 223–233.
Kadi, A. A., El-Brollosy, N. R., Al-Deeb, O. A., Habib, E. E., Ibrahim, T. M. & El-Emam, A. A. (2007). *Eur. J. Med. Chem.* **42**, 235–242.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Mickevičius, V., Vaickelionienė, R. & Sapijanskaitė, B. (2009). *Chem. Heterocycl. C.* **45**, 215–218.
Ramazani, A., Abdian, B., Nasrabadi, F. Z. & Rouhani, M. (2013). *Phosphorus Sulfur Silicon*, **188**, 642–648.
Ramazani, A., Nasrabadi, F. Z. & Ahmadi, Y. (2011). *Helv. Chim. Acta*, **94**, 1024–1029.
Rigaku OD. (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Shirote, P. J. & Bhatia, M. S. (2010). *Chin. J. Chem.* **28**, 1429–1436.
Vasil'ev, N. V., Romanov, D. V., Bazhenov, A. A., Lyssenko, K. A. & Zatonsky, G. V. (2007). *J. Fluor. Chem.* **128**, 740–747.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Wolkenberg, S. E. & Boger, D. L. (2002). *J. Org. Chem.* **67**, 7361–7364.
Won, C., Shen, X., Mashiguchi, K., Zheng, Z., Dai, X., Cheng, Y., Kasahara, H., Kamiya, Y., Chory, J. & Zhao, Y. (2011). *Proc. Natl Acad. Sci. USA*, **108**, 18518–18523.
Yuan, Z. Q., Ishikawa, H. & Boger, D. L. (2005). *Org. Lett.* **7**, 741–744.
Zampieri, D., Mamolo, M. G., Laurini, E., Fermeglia, M., Posocco, P., Pricl, S., Banfi, E., Scialino, G. & Vio, L. (2009). *Bioorg. Med. Chem.* **17**, 4693–4707.
Zheng, Zh., Liu, O., Kim, W., Tharmalingam, N., Fuchs, B. B. & Mylonakis, E. (2018). *Future Med. Chem.* **10**, 283–296.

full crystallographic data

IUCrData (2019). **4**, x191532 [https://doi.org/10.1107/S2414314619015323]

5-(3-Hydroxyphenyl)-1,3,4-oxadiazole-2(3*H*)-thione hemihydrate

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5-(3-Hydroxyphenyl)-1,3,4-oxadiazole-2(3*H*)-thione hemihydrate

Crystal data

$2C_8H_6N_2O_2S·H_2O$
M_r = 406.43
Monoclinic, *I*2/*a*
a = 16.3881 (12) Å
b = 4.6912 (3) Å
c = 22.4928 (18) Å
β = 97.512 (7)°
V = 1714.4 (2) Å^3
Z = 4
F(000) = 840
D_x = 1.575 Mg m^{-3}
Cu *Kα* radiation, *λ* = 1.54184 Å
Cell parameters from 1053 reflections
θ = 5.4–74.2°
μ = 3.17 mm^{-1}
T = 293 K
Block, colourless
0.4 × 0.28 × 0.2 mm

Data collection

Rigaku Xcalibur Ruby diffractometer
Detector resolution: 10.2576 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2015)
T_{min} = 0.953, T_{max} = 1.000
5850 measured reflections
1767 independent reflections
1256 reflections with $I > 2\sigma(I)$
R_{int} = 0.061
θ_{max} = 76.1°, θ_{min} = 4.0°
h = −18→20
k = −4→5
l = −27→27

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.117
S = 1.04
1767 reflections
128 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Special details

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

Refinement. The hydrogen atom of the water molecule was located from a difference electron-density map and was refined with O—H = 0.85 (4) Å, and U_{iso}(H) = 1.3U_{eq}(O).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.67502 (4)	1.34393 (15)	0.35767 (3)	0.0449 (2)
O1	0.55444 (11)	0.9588 (4)	0.35221 (8)	0.0373 (4)
O2	0.32072 (15)	0.0756 (5)	0.42672 (10)	0.0555 (6)
H2	0.290571	−0.045956	0.409275	0.083*
O1W	0.750000	1.3852 (8)	0.500000	0.0597 (9)
N1	0.60967 (15)	1.0310 (5)	0.44201 (11)	0.0447 (6)
H1	0.640309	1.100099	0.472576	0.054*
N0AA	0.55104 (15)	0.8229 (5)	0.44618 (11)	0.0452 (6)
C2	0.51961 (16)	0.7884 (6)	0.39152 (11)	0.0361 (6)
C3	0.45590 (16)	0.5862 (5)	0.36792 (12)	0.0365 (6)
C8	0.41731 (17)	0.4239 (6)	0.40779 (13)	0.0392 (6)
H8	0.431399	0.446199	0.448938	0.047*
C1	0.61390 (16)	1.1129 (6)	0.38633 (12)	0.0380 (6)
C7	0.35775 (17)	0.2289 (6)	0.38559 (13)	0.0401 (6)
C4	0.43517 (18)	0.5516 (6)	0.30612 (13)	0.0435 (7)
H4	0.461017	0.659969	0.279433	0.052*
C6	0.33699 (18)	0.1922 (6)	0.32463 (13)	0.0447 (7)
H6	0.297161	0.059244	0.310210	0.054*
C5	0.37544 (19)	0.3532 (7)	0.28508 (13)	0.0480 (7)
H5	0.361217	0.328550	0.244007	0.058*
H1W	0.742 (3)	1.497 (8)	0.4702 (18)	0.086 (14)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0410 (4)	0.0408 (4)	0.0533 (4)	−0.0028 (3)	0.0071 (3)	0.0054 (3)
O1	0.0366 (9)	0.0366 (9)	0.0384 (10)	−0.0010 (8)	0.0037 (7)	0.0026 (8)
O2	0.0563 (13)	0.0618 (15)	0.0488 (12)	−0.0194 (10)	0.0080 (10)	−0.0006 (10)
O1W	0.078 (2)	0.055 (2)	0.0451 (18)	0.000	0.0046 (17)	0.000
N1	0.0464 (14)	0.0494 (14)	0.0372 (12)	−0.0080 (11)	0.0013 (10)	−0.0030 (11)
N0AA	0.0479 (14)	0.0479 (14)	0.0402 (12)	−0.0076 (11)	0.0074 (10)	0.0005 (11)
C2	0.0390 (14)	0.0355 (13)	0.0350 (13)	0.0023 (10)	0.0094 (11)	0.0024 (11)
C3	0.0350 (13)	0.0328 (13)	0.0426 (15)	0.0039 (10)	0.0080 (11)	0.0008 (10)
C8	0.0390 (14)	0.0396 (15)	0.0391 (14)	0.0003 (11)	0.0054 (11)	−0.0018 (11)
C1	0.0346 (13)	0.0357 (14)	0.0433 (15)	0.0035 (10)	0.0035 (11)	−0.0007 (11)
C7	0.0381 (14)	0.0386 (14)	0.0453 (15)	0.0012 (11)	0.0122 (12)	0.0012 (12)
C4	0.0464 (16)	0.0427 (15)	0.0418 (15)	−0.0032 (12)	0.0072 (12)	0.0026 (12)
C6	0.0402 (15)	0.0429 (16)	0.0503 (17)	−0.0027 (12)	0.0034 (12)	−0.0066 (13)
C5	0.0516 (16)	0.0518 (17)	0.0395 (15)	−0.0033 (14)	0.0013 (12)	−0.0033 (14)

Geometric parameters (Å, º)

S1—C1	1.662 (3)	C2—C3	1.458 (4)
O1—C1	1.366 (3)	C3—C8	1.390 (4)
O1—C2	1.371 (3)	C3—C4	1.396 (4)

O2—C7	1.374 (3)	C8—C7	1.382 (4)
O2—H2	0.8200	C8—H8	0.9300
O1W—H1W	0.85 (4)	C7—C6	1.380 (4)
O1W—H1W^{i}	0.85 (4)	C4—C5	1.388 (4)
N1—C1	1.321 (4)	C4—H4	0.9300
N1—N0AA	1.381 (3)	C6—C5	1.380 (4)
N1—H1	0.8600	C6—H6	0.9300
N0AA—C2	1.280 (4)	C5—H5	0.9300
C1—O1—C2	105.8 (2)	N1—C1—O1	104.9 (2)
C7—O2—H2	109.5	N1—C1—S1	131.8 (2)
H1W—O1W—H1W^{i}	104 (6)	O1—C1—S1	123.3 (2)
C1—N1—N0AA	113.2 (2)	O2—C7—C6	122.0 (3)
C1—N1—H1	123.4	O2—C7—C8	117.1 (3)
N0AA—N1—H1	123.4	C6—C7—C8	120.8 (3)
C2—N0AA—N1	102.7 (2)	C5—C4—C3	119.1 (3)
N0AA—C2—O1	113.4 (2)	C5—C4—H4	120.5
N0AA—C2—C3	127.7 (2)	C3—C4—H4	120.5
O1—C2—C3	118.9 (2)	C7—C6—C5	119.9 (3)
C8—C3—C4	120.4 (3)	C7—C6—H6	120.1
C8—C3—C2	119.1 (2)	C5—C6—H6	120.1
C4—C3—C2	120.5 (2)	C6—C5—C4	120.5 (3)
C7—C8—C3	119.2 (3)	C6—C5—H5	119.7
C7—C8—H8	120.4	C4—C5—H5	119.7
C3—C8—H8	120.4		

Symmetry code: (i) −*x*+3/2, *y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1*W*	0.86	2.26	2.995 (3)	143
N1—H1···O2^{ii}	0.86	2.42	3.064 (3)	133
O1*W*—H1*W*···S1	0.85 (4)	2.72 (4)	3.2814 (9)	125 (3)
O2—H2···S1^{iii}	0.82	2.51	3.319 (2)	168

Symmetry codes: (ii) −*x*+1, −*y*+1, −*z*+1; (iii) *x*−1/2, −*y*+1, *z*.