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6-Nitro-1,3-benzoxazole-2(3*H*)-thione

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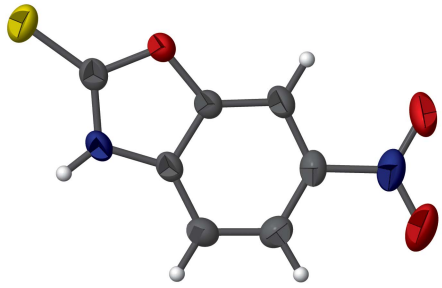
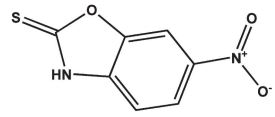
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_7H_4N_2O_3S$, the dihedral angle between the fused ring system (r.m.s. deviation = 0.008 Å) and the nitro group at the 6-position is 7.3 (2)°. In the crystal, bifurcated N—H···(O,O) hydrogen bonds link the molecules into [010] chains. The chains are cross-linked by π–π stacking interactions to form (001) sheets.

3D view



Chemical scheme



Structure description

The mono-nitration of some benzimidazole derivatives has been reported (Benchidmi *et al.*, 1995; El Kihel *et al.*, 1999). In this work, the nitration of benzoxazole-2-thione has been carried out and the crystal structure determined to establish the location of the NO_2 group (the 5- or 6-position) in the product (Fig. 1).

The plane of the fused ring system (r.m.s. deviation = 0.008 Å) is slightly inclined to the plane of the nitro group [dihedral angle = 7.3 (2)°]. In the crystal, the molecules are linked by bifurcated N—H···(O,O) hydrogen bonds (Table 1) to form [010] chains (Fig. 2). The chains are cross-linked by weak aromatic π–π stacking between the benzene ring and oxazole ring to form (001) sheets, the inter-centroid distance being 3.646 (3) Å (Fig. 3).

Synthesis and crystallization

To benzoxazole-2-thione (0.025 mol) in 92% H_2SO_4 (10 ml) was added dropwise with stirring a cooled mixture of 42% HNO_3 (2.5 ml) and 92% H_2SO_4 (1 ml). The resulting mixture was allowed to stand for 1 h at 273–278 K and then poured in an ice–water mixture (50 g – 50 g). After addition of NaCl (10 g), the solution, maintained at 273–

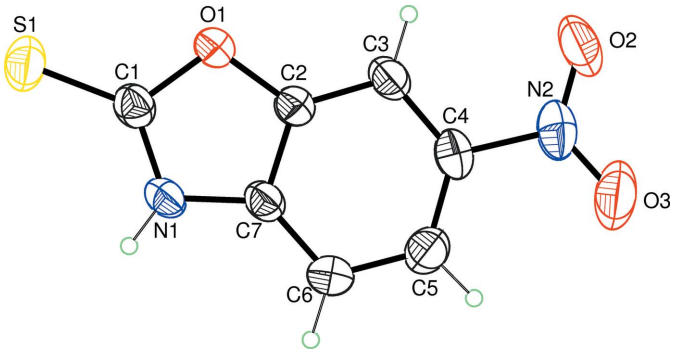


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

283 K, deposited solid material, which was filtered off, washed with cold water and dissolved in hot water. The pH of the resulting solution was adjusted to 7.5–8 with 3 *M* NH_3. 6-Nitrobenzoxazole-2-thione was filtered off and recrystallized several times from methanol solution to give yellow blocks.

Refinement

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

Acknowledgements

The authors thank the Faculty of Science, Mohammed V University in Rabat, Morocco for the X-ray measurements and Chouaib Doukkali University (El Jadida Morocco) for support.

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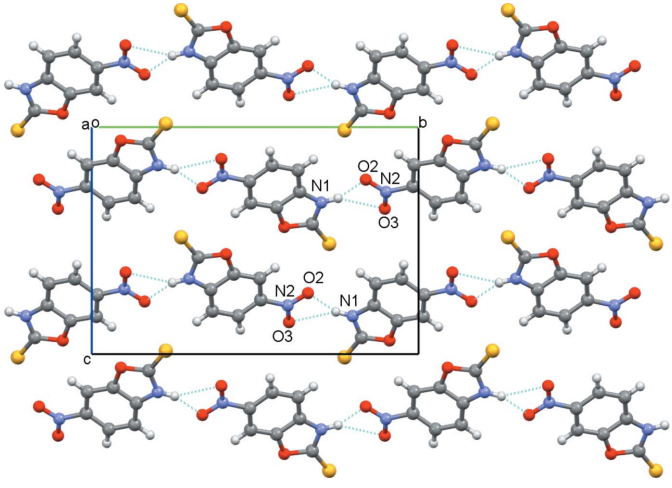

Figure 2
Projection of the title compound structure onto the (100) plane, showing molecules connected by hydrogen bonds (dashed blue lines).

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.84	2.41	3.068 (3)	135
N1—H1···O3^{i}	0.84	2.36	3.137 (3)	154

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_4N_2O_3S$
M_r	196.18
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	296
a, b, c (Å)	4.576 (4), 15.755 (13), 11.134 (9)
β (°)	100.45 (3)
V (Å^3)	789.3 (11)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.38
Crystal size (mm)	0.35 × 0.28 × 0.21
Data collection	
Diffractometer	Bruker D8 VENTURE Super DUO
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.668, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17038, 1870, 1538
R_{int}	0.032
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.658
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.110, 1.03
No. of reflections	1870
No. of parameters	118
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.26

Computer programs: *APEX3* (Bruker, 2016), *SAINT* (Bruker, 2016), *SHELXTL2014* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *WinGX* and *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

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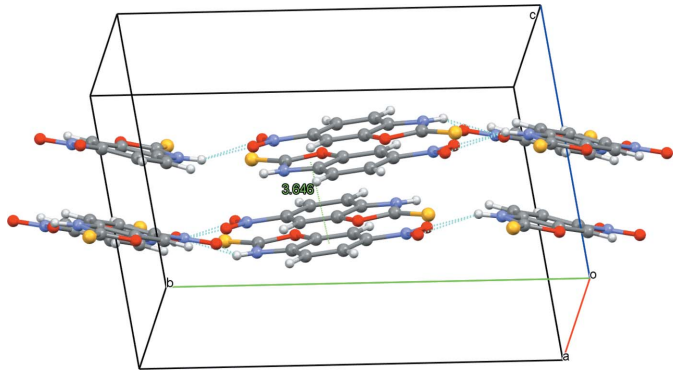

Figure 3
Crystal packing for the title compound showing molecules linked by hydrogen bonds (dashed blue lines) and π–π interactions (green lines).

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full crystallographic data

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Crystal data

$C_7H_4N_2O_3S$
M_r = 196.18
Monoclinic, $P2_1/n$
a = 4.576 (4) Å
b = 15.755 (13) Å
c = 11.134 (9) Å
β = 100.45 (3)°
V = 789.3 (11) Å^3
Z = 4
$F(000)$ = 400
D_x = 1.651 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1870 reflections
θ = 2.6–27.9°
μ = 0.38 mm^{-1}
T = 296 K
Block, yellow
0.35 × 0.28 × 0.21 mm

Data collection

Bruker D8 VENTURE Super DUO diffractometer
Radiation source: INCOATEC IμS micro-focus source
HELIOS mirror optics monochromator
Detector resolution: 10.4167 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause et al., 2015)
T_{min} = 0.668, T_{max} = 0.747
17038 measured reflections
1870 independent reflections
1538 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 27.9°, θ_{min} = 2.6°
h = −6→6
k = −20→20
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.110
S = 1.03
1870 reflections
118 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.3797P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	1.18641 (11)	0.72656 (3)	0.51464 (5)	0.05120 (19)
O1	0.8774 (3)	0.58902 (7)	0.44023 (12)	0.0400 (3)
O2	0.2383 (5)	0.33844 (10)	0.26846 (17)	0.0859 (7)
O3	−0.1051 (4)	0.39654 (11)	0.1403 (2)	0.0766 (6)
N1	0.7184 (3)	0.70175 (9)	0.33226 (14)	0.0374 (3)
H1	0.688902	0.753157	0.314460	0.045*
N2	0.1258 (4)	0.40037 (11)	0.21413 (16)	0.0500 (4)
C1	0.9228 (4)	0.67448 (11)	0.42680 (16)	0.0360 (4)
C2	0.6377 (4)	0.56547 (10)	0.35289 (15)	0.0325 (4)
C3	0.5143 (4)	0.48630 (11)	0.33371 (16)	0.0383 (4)
H3	0.586671	0.439175	0.380032	0.046*
C4	0.2721 (4)	0.48278 (11)	0.23917 (17)	0.0379 (4)
C5	0.1602 (4)	0.55204 (13)	0.16860 (18)	0.0429 (4)
H5	−0.004636	0.545447	0.106807	0.051*
C6	0.2929 (4)	0.63094 (12)	0.18979 (18)	0.0425 (4)
H6	0.223268	0.678035	0.142831	0.051*
C7	0.5340 (4)	0.63613 (10)	0.28427 (16)	0.0331 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0455 (3)	0.0438 (3)	0.0604 (4)	−0.0078 (2)	−0.0005 (2)	−0.0129 (2)
O1	0.0442 (7)	0.0267 (6)	0.0445 (7)	0.0005 (5)	−0.0042 (5)	0.0015 (5)
O2	0.1327 (18)	0.0374 (8)	0.0735 (12)	−0.0331 (10)	−0.0189 (11)	0.0090 (8)
O3	0.0572 (10)	0.0574 (10)	0.1077 (15)	−0.0142 (8)	−0.0056 (10)	−0.0284 (10)
N1	0.0369 (8)	0.0232 (6)	0.0508 (9)	0.0024 (6)	0.0043 (6)	0.0038 (6)
N2	0.0596 (11)	0.0418 (9)	0.0495 (10)	−0.0154 (8)	0.0120 (8)	−0.0138 (8)
C1	0.0364 (9)	0.0285 (8)	0.0437 (10)	0.0021 (7)	0.0093 (7)	−0.0027 (7)
C2	0.0345 (8)	0.0279 (8)	0.0343 (8)	0.0019 (6)	0.0044 (7)	−0.0001 (6)
C3	0.0493 (10)	0.0257 (8)	0.0392 (9)	−0.0012 (7)	0.0061 (8)	0.0015 (7)
C4	0.0428 (9)	0.0308 (8)	0.0419 (10)	−0.0062 (7)	0.0125 (8)	−0.0071 (7)
C5	0.0378 (9)	0.0453 (10)	0.0432 (10)	0.0001 (8)	0.0009 (8)	−0.0049 (8)
C6	0.0422 (10)	0.0351 (9)	0.0471 (10)	0.0049 (7)	−0.0005 (8)	0.0053 (8)
C7	0.0332 (8)	0.0248 (7)	0.0418 (9)	0.0023 (6)	0.0078 (7)	0.0015 (6)

Geometric parameters (Å, º)

S1—C1	1.630 (2)	C2—C3	1.370 (3)
O1—C1	1.375 (2)	C2—C7	1.384 (2)
O1—C2	1.378 (2)	C3—C4	1.384 (3)
O2—N2	1.212 (3)	C3—H3	0.9300
O3—N2	1.217 (3)	C4—C5	1.387 (3)
N1—C1	1.346 (2)	C5—C6	1.385 (3)
N1—C7	1.379 (2)	C5—H5	0.9300
N1—H1	0.8389	C6—C7	1.382 (3)

N2—C4	1.464 (2)	C6—H6	0.9300
C1—O1—C2	107.67 (13)	C2—C3—H3	123.0
C1—N1—C7	110.69 (15)	C4—C3—H3	123.0
C1—N1—H1	123.5	C3—C4—C5	124.17 (17)
C7—N1—H1	124.8	C3—C4—N2	117.11 (17)
O2—N2—O3	122.37 (19)	C5—C4—N2	118.72 (18)
O2—N2—C4	118.72 (19)	C6—C5—C4	120.28 (18)
O3—N2—C4	118.91 (19)	C6—C5—H5	119.9
N1—C1—O1	107.49 (14)	C4—C5—H5	119.9
N1—C1—S1	129.98 (14)	C7—C6—C5	116.58 (17)
O1—C1—S1	122.54 (13)	C7—C6—H6	121.7
C3—C2—O1	127.43 (15)	C5—C6—H6	121.7
C3—C2—C7	123.77 (17)	N1—C7—C6	133.39 (16)
O1—C2—C7	108.80 (15)	N1—C7—C2	105.34 (16)
C2—C3—C4	113.92 (16)	C6—C7—C2	121.27 (16)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{i}	0.84	2.41	3.068 (3)	135
N1—H1···O3^{i}	0.84	2.36	3.137 (3)	154

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