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6-Nitro-1,3-benzothiazole-2(3H)-thione

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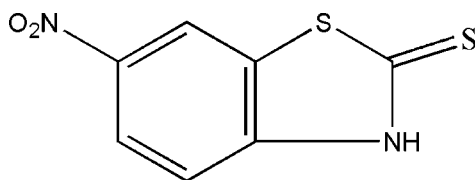
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 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.063; wR factor = 0.165; data-to-parameter ratio = 12.1.

In the title molecule, $\text{C}_7\text{H}_4\text{N}_2\text{O}_2\text{S}_2$, the nitro group is twisted by $5.5(1)^\circ$ from the plane of the attached benzene ring. In the crystal, $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds link pairs of molecules into inversion dimers, which are linked by weak $\text{C}-\text{H}\cdots\text{O}$ interactions into sheets parallel to (101). The crystal packing exhibits short intermolecular $\text{S}\cdots\text{O}$ contacts of $3.054(4)$ Å and $\pi-\pi$ interactions of $3.588(5)$ Å between the centroids of the five- and six-membered rings of neighbouring molecules.

Related literature

For coordination compounds based on 2-mercapto-6-nitro-benzothiazole ligands, see: Ma *et al.* (2003*a,b*, 2004). For the structure of the related compound 2-mercapto-benzothiazole, see: Chesick & Donohue (1971).



Experimental

Crystal data

 $\text{C}_7\text{H}_4\text{N}_2\text{O}_2\text{S}_2$
 $M_r = 212.24$
 Monoclinic, $P2_1/n$
 $a = 3.8645(2)$ Å
 $b = 26.345(2)$ Å
 $c = 7.8961(4)$ Å

 $\beta = 92.509(1)^\circ$
 $V = 803.14(9)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation

 $\mu = 0.62$ mm⁻¹
 $T = 298$ K
 $0.40 \times 0.35 \times 0.27$ mm

Data collection

 Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2007)
 $T_{\min} = 0.789$, $T_{\max} = 0.850$
 4092 measured reflections
 1425 independent reflections
 1104 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.109$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.063$
 $wR(F^2) = 0.165$
 $S = 1.04$
 1425 reflections
 118 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.45$ e Å⁻³
 $\Delta\rho_{\min} = -0.42$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{S2}^{\text{i}}$	0.86	2.45	3.271 (3)	160
$\text{C4}-\text{H4}\cdots\text{O1}^{\text{ii}}$	0.93	2.60	3.285 (6)	131

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

Data collection: SMART (Bruker, 2007); cell refinement: SAINT-Plus (Bruker, 2007); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5367).

References

- Bruker (2007). SMART, SAINT-Plus and SADABS. Bruker AXS Inc., Wisconsin, USA.
 Chesick, J. P. & Donohue, J. (1971). *Acta Cryst.* **B27**, 1441–1444.
 Ma, C. L., Jiang, Q. & Zhang, R. F. (2003*a*). *Can. J. Chem.* **81**, 825–831.
 Ma, C. L., Jiang, Q. & Zhang, R. F. (2003*b*). *Appl. Organomet. Chem.* **17**, 623–630.
 Ma, C. L., Jiang, Q. & Zhang, R. F. (2004). *Polyhedron*, **23**, 779–786.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supporting information

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

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S1. Comment

Metal-organic supramolecular compounds have received much attention due to their structural diversities and potential applications as new materials. The ligand 2-mercapto-6-nitrobenzothiazole (MNBT) is excellent in building supramolecular structures. However, to our best knowledge, only a few Ag(I)-MNBT (MNBT = 2-mercapto-6-nitrobenzothiazole) framework structures have been reported (Ma *et al.*, 2003*a,b*; 2004). The title compound, (I), was unexpectedly obtained when we tried to synthesize Ag(I)-MNBT complexes containing bis(diphenylphosphino)methane.

In (I) (Fig. 1), the nitro group is twisted at 5.5 (1)° from the plane of the attached benzene ring. Intermolecular N—H···S hydrogen bonds (Table 1) link two molecules into centrosymmetric dimer, and weak C—H···O interactions (Table 1) link further these dimers into sheets parallel to (101). The hydrogen bond N—H···S is similar to that reported for 2-mercapto-benzothiazole (Chesick & Donohue, 1971). The crystal packing (Fig. 2) exhibits short intermolecular S···O contacts of 3.054 (4) Å and π – π interactions proved by short distance of 3.588 (5) Å between the centroids of the five- and six-membered rings from the neighbouring molecules.

S2. Experimental

A mixture of AgCl (0.2 mmol) and bis(diphenylphosphino)methane (0.2 mmol) in MeOH and CH₂Cl₂ (10 mL, *v/v* = 1:1) was stirred for 3 h. The insoluble residues were removed by filtration. The filtrate was then evaporated slowly at room temperature for a week to yield colourless crystalline product.

The title compound was prepared by dissolving 0.0587 g colourless product mentioned above in MeOH and CH₂Cl₂ (10 mL, *v/v* = 3:7), adding 2-mercapto-6-nitrobenzothiazole (0.2 mmol) into the solution, stirring for 4 h. Subsequent slow evaporation of the yellow filtrate resulted in the formation of yellow crystals.

S3. Refinement

All H atoms were geometrically positioned [C—H 0.93 Å; N—H 0.86 Å], and included in the final refinement in the riding model approximation, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ of the parent atom.

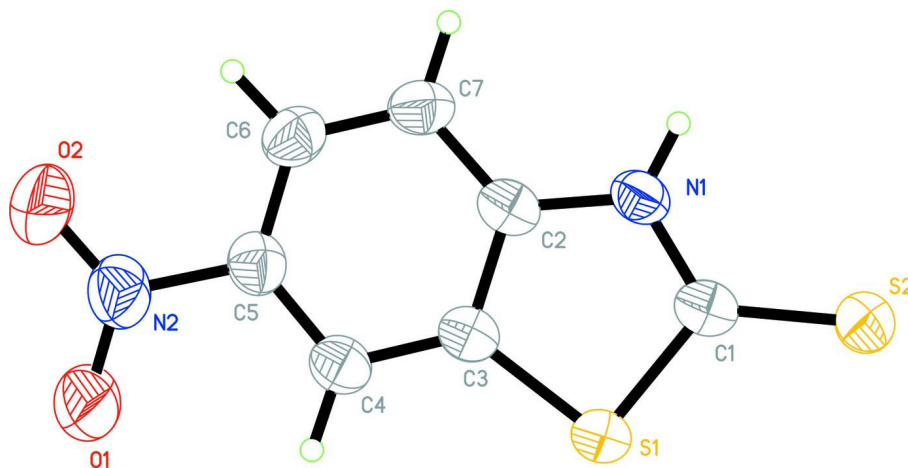


Figure 1

The molecular structure of (I) showing the atomic numbering scheme and displacement ellipsoids drawn at the 50% probability level.

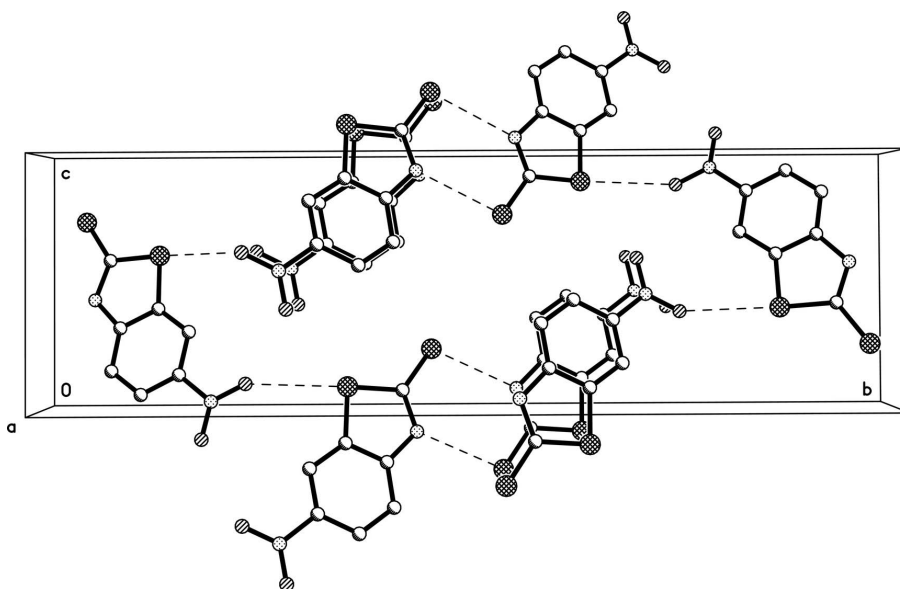


Figure 2

A portion of the crystal packing viewed approximately along the *a* axis. Dashed lines indicate short N...S and O...S contacts. H atoms omitted for clarity.

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

Crystal data

$C_7H_4N_2O_2S_2$

$M_r = 212.24$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 3.8645\ (2)\ \text{\AA}$

$b = 26.345\ (2)\ \text{\AA}$

$c = 7.8961\ (4)\ \text{\AA}$

$\beta = 92.509\ (1)^\circ$

$V = 803.14\ (9)\ \text{\AA}^3$

$Z = 4$

$F(000) = 432$

$D_x = 1.755\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1148 reflections

$\theta = 2.7\text{--}23.7^\circ$

$\mu = 0.62\ \text{mm}^{-1}$

$T = 298$ K $0.40 \times 0.35 \times 0.27$ mm
 Block, colourless

Data collection

Bruker SMART CCD area-detector diffractometer Radiation source: fine-focus sealed tube Graphite monochromator phi and ω scans Absorption correction: multi-scan (SADABS; Bruker, 2007) $T_{\min} = 0.789$, $T_{\max} = 0.850$	4092 measured reflections 1425 independent reflections 1104 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.109$ $\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 2.7^\circ$ $h = -4 \rightarrow 4$ $k = -30 \rightarrow 31$ $l = -9 \rightarrow 6$
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Refinement

Refinement on F^2 Least-squares matrix: full $R[F^2 > 2\sigma(F^2)] = 0.063$ $wR(F^2) = 0.165$ $S = 1.04$ 1425 reflections 118 parameters 0 restraints Primary atom site location: structure-invariant direct methods	Secondary atom site location: difference Fourier map Hydrogen site location: inferred from neighbouring sites H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.0915P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.45 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.42 \text{ e } \text{\AA}^{-3}$
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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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.2970 (8)	0.05823 (12)	0.4296 (4)	0.0383 (8)
H1	0.2434	0.0278	0.3985	0.046*
N2	0.8798 (11)	0.20738 (15)	0.0513 (6)	0.0559 (10)
O1	0.9284 (13)	0.24753 (15)	0.1198 (5)	0.1031 (17)
O2	0.9722 (12)	0.19831 (14)	-0.0880 (5)	0.0844 (13)
S1	0.3759 (3)	0.13687 (4)	0.60511 (13)	0.0414 (4)
S2	0.0806 (3)	0.04194 (4)	0.73917 (14)	0.0450 (4)
C1	0.2447 (10)	0.07491 (14)	0.5857 (5)	0.0360 (9)
C2	0.4399 (10)	0.09190 (14)	0.3216 (5)	0.0350 (9)
C3	0.5018 (10)	0.13824 (14)	0.3978 (5)	0.0350 (9)
C4	0.6477 (10)	0.17709 (15)	0.3110 (5)	0.0403 (10)
H4	0.6936	0.2085	0.3610	0.048*
C5	0.7219 (11)	0.16726 (15)	0.1476 (5)	0.0410 (10)
C6	0.6620 (11)	0.12160 (16)	0.0691 (6)	0.0444 (10)

H6	0.7212	0.1168	-0.0426	0.053*
C7	0.5160 (11)	0.08351 (16)	0.1556 (5)	0.0429 (10)
H7	0.4684	0.0524	0.1041	0.052*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.043 (2)	0.0305 (17)	0.0407 (19)	-0.0046 (14)	-0.0031 (16)	-0.0022 (15)
N2	0.066 (3)	0.043 (2)	0.060 (3)	0.0034 (18)	0.013 (2)	0.010 (2)
O1	0.182 (5)	0.045 (2)	0.088 (3)	-0.028 (2)	0.066 (3)	-0.007 (2)
O2	0.129 (4)	0.067 (2)	0.060 (2)	-0.016 (2)	0.038 (2)	0.008 (2)
S1	0.0487 (7)	0.0354 (6)	0.0401 (6)	-0.0059 (4)	0.0029 (5)	-0.0051 (4)
S2	0.0497 (7)	0.0425 (6)	0.0427 (6)	-0.0076 (5)	0.0023 (5)	0.0004 (4)
C1	0.028 (2)	0.035 (2)	0.043 (2)	0.0026 (16)	-0.0063 (17)	-0.0030 (17)
C2	0.029 (2)	0.033 (2)	0.042 (2)	0.0016 (16)	-0.0089 (17)	-0.0010 (17)
C3	0.031 (2)	0.032 (2)	0.041 (2)	0.0034 (15)	-0.0022 (17)	-0.0017 (16)
C4	0.042 (2)	0.033 (2)	0.045 (2)	0.0029 (17)	0.0004 (19)	-0.0005 (17)
C5	0.040 (2)	0.037 (2)	0.047 (2)	0.0041 (17)	0.0051 (19)	0.0043 (19)
C6	0.050 (3)	0.047 (2)	0.035 (2)	0.005 (2)	0.0008 (19)	-0.0003 (19)
C7	0.049 (3)	0.041 (2)	0.038 (2)	0.0025 (18)	-0.0031 (19)	-0.0065 (19)

Geometric parameters (Å, °)

N1—C1	1.332 (5)	C2—C7	1.373 (5)
N1—C2	1.364 (5)	C2—C3	1.378 (5)
N1—H1	0.8600	C3—C4	1.367 (5)
N2—O2	1.196 (5)	C4—C5	1.359 (5)
N2—O1	1.199 (5)	C4—H4	0.9300
N2—C5	1.452 (5)	C5—C6	1.368 (6)
S1—C1	1.714 (4)	C6—C7	1.351 (6)
S1—C3	1.728 (4)	C6—H6	0.9300
S2—C1	1.641 (4)	C7—H7	0.9300
C1—N1—C2	116.5 (3)	C4—C3—S1	129.0 (3)
C1—N1—H1	121.8	C2—C3—S1	110.2 (3)
C2—N1—H1	121.8	C5—C4—C3	116.3 (4)
O2—N2—O1	123.0 (4)	C5—C4—H4	121.9
O2—N2—C5	119.1 (4)	C3—C4—H4	121.9
O1—N2—C5	117.9 (4)	C4—C5—C6	124.0 (4)
C1—S1—C3	91.69 (18)	C4—C5—N2	118.0 (4)
N1—C1—S2	126.0 (3)	C6—C5—N2	118.0 (4)
N1—C1—S1	109.9 (3)	C7—C6—C5	119.4 (4)
S2—C1—S1	124.1 (2)	C7—C6—H6	120.3
N1—C2—C7	127.0 (4)	C5—C6—H6	120.3
N1—C2—C3	111.7 (3)	C6—C7—C2	118.3 (4)
C7—C2—C3	121.3 (4)	C6—C7—H7	120.8
C4—C3—C2	120.8 (4)	C2—C7—H7	120.8

C2—N1—C1—S2	-179.4 (3)	S1—C3—C4—C5	179.8 (3)
C2—N1—C1—S1	0.5 (4)	C3—C4—C5—C6	-0.6 (6)
C3—S1—C1—N1	-0.3 (3)	C3—C4—C5—N2	-179.5 (4)
C3—S1—C1—S2	179.6 (3)	O2—N2—C5—C4	174.2 (4)
C1—N1—C2—C7	-179.7 (4)	O1—N2—C5—C4	-1.9 (7)
C1—N1—C2—C3	-0.4 (5)	O2—N2—C5—C6	-4.8 (7)
N1—C2—C3—C4	179.4 (4)	O1—N2—C5—C6	179.2 (5)
C7—C2—C3—C4	-1.3 (6)	C4—C5—C6—C7	1.0 (7)
N1—C2—C3—S1	0.2 (4)	N2—C5—C6—C7	179.8 (4)
C7—C2—C3—S1	179.5 (3)	C5—C6—C7—C2	-1.4 (6)
C1—S1—C3—C4	-179.1 (4)	N1—C2—C7—C6	-179.2 (4)
C1—S1—C3—C2	0.1 (3)	C3—C2—C7—C6	1.6 (6)
C2—C3—C4—C5	0.7 (6)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...S2 ⁱ	0.86	2.45	3.271 (3)	160
C4—H4...O1 ⁱⁱ	0.93	2.60	3.285 (6)	131

Symmetry codes: (i) $-x, -y, -z+1$; (ii) $x-1/2, -y+1/2, z+1/2$.