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5-(4-Bromo-2-nitrophenyl)-1,3,4-thiadiazol-2-amine

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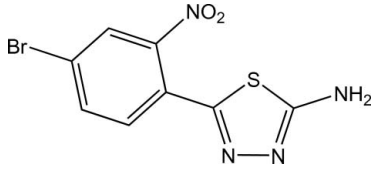
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.049; wR factor = 0.104; data-to-parameter ratio = 12.6.

The title compound, $C_8H_5BrN_4O_2S$, was synthesized by the reaction of 4-bromo-2-nitrobenzoic acid with thiosemicarbazide. The dihedral angle between the thiadiazole and benzene rings is 40.5 (2)°. In the crystal, the strongest N—H···N intermolecular hydrogen bond, between the amine group and one thiadiazole N atom, forms centrosymmetric dimers. The other amine H atom extends the supramolecular network, forming an N—H···N contact with the other thiadiazole N atom.

Related literature

For the biological activity of 1,3,4-thiadiazole derivatives, see: Nakagawa *et al.* (1996); Wang *et al.* (1999).



Experimental

Crystal data

$C_8H_5BrN_4O_2S$
M_r = 301.13
Monoclinic, $P2_1/c$
a = 11.231 (2) Å
b = 9.2580 (19) Å
c = 10.868 (2) Å
β = 113.08 (3)°
V = 1039.6 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.14 mm^{-1}
T = 293 K
0.20 × 0.10 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.491, T_{max} = 0.682
3909 measured reflections
1920 independent reflections
1409 reflections with $I > 2\sigma(I)$
R_{int} = 0.116
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.104
S = 1.01
1920 reflections
152 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.97 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4B···N3^{i}	0.79 (7)	2.25 (7)	3.014 (6)	165 (7)
N4—H4C···N2^{ii}	0.80 (6)	2.34 (6)	3.103 (6)	161 (6)

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1989); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo,1995); 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: *SHELXL97*.

The authors thank Professor Hua-qin Wang of the Analysis Centre, Nanjing University, for carrying out the X-ray crystallographic analysis.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2371).

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supporting information

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S1. Comment

1,3,4-Thiadiazole derivatives represent an interesting class of compounds possessing a broad spectrum of biological activities (Nakagawa *et al.*, 1996). These compounds are known to exhibit diverse biological activities, such as insecticidal and fungicidal activities (Wang *et al.*, 1999). Here we report the crystal structure of the title compound, a new thiadiazole. In the molecular structure (Fig. 1) the bond lengths and angles are within normal ranges. Thiadiazole ring C8/S/C7/N2/N3 is planar, and the mean deviation from the plane is 0.0046 Å. The dihedral angle between the thiadiazole and benzene rings is 40.5 (2)°. In the crystal structure, the strongest N—H···N intermolecular contact (first entry in the hydrogen bonds Table) forms centrosymmetric dimers in the crystal (top molecules in Fig. 2). This pattern is the primary supramolecular structure for this compound. The other hydrogen bond (entry 2) is comparatively weak, and extends the primary pattern to a three-dimensional network, which may be effective in the stabilization of the crystal structure.

S2. Experimental

4-Bromo-2-nitrobenzoic acid (2 mmol) and thiosemicarbazide (5 mmol) were mixed in a 25 ml flask, and kept in the oil bath at 90 °C for 6 h. After cooling, the crude product precipitated and was filtered. Pure compound was obtained by crystallization from ethanol (20 ml). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetone solution.

S3. Refinement

All H atoms bonded to the C atoms were placed geometrically at the distances of 0.93 Å and included in the refinement in riding motion approximation with U_{iso}(H) = 1.2U_{eq}(carrier C atom). Amine H atoms H4B and H4C were found in a difference map and refined freely, with U_{iso}(H) = 1.2U_{eq}(N4).

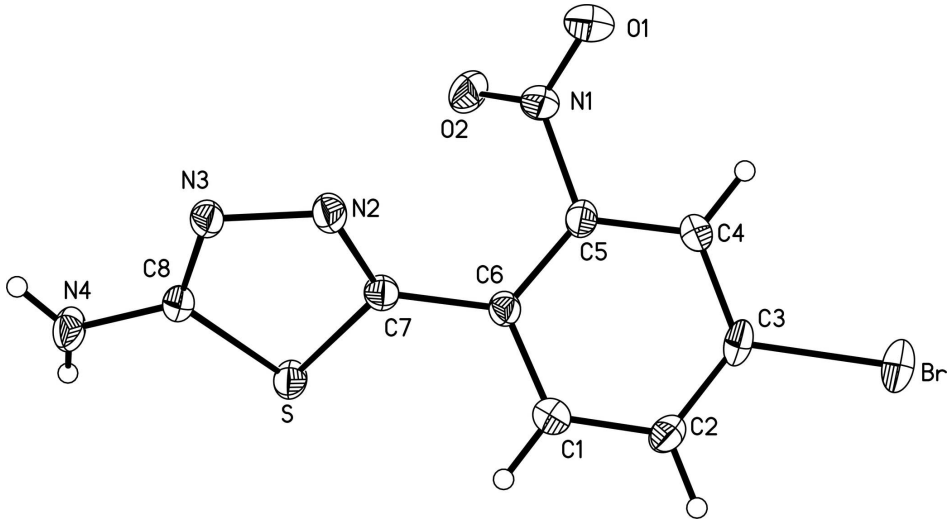

Figure 1

A view of the molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level.

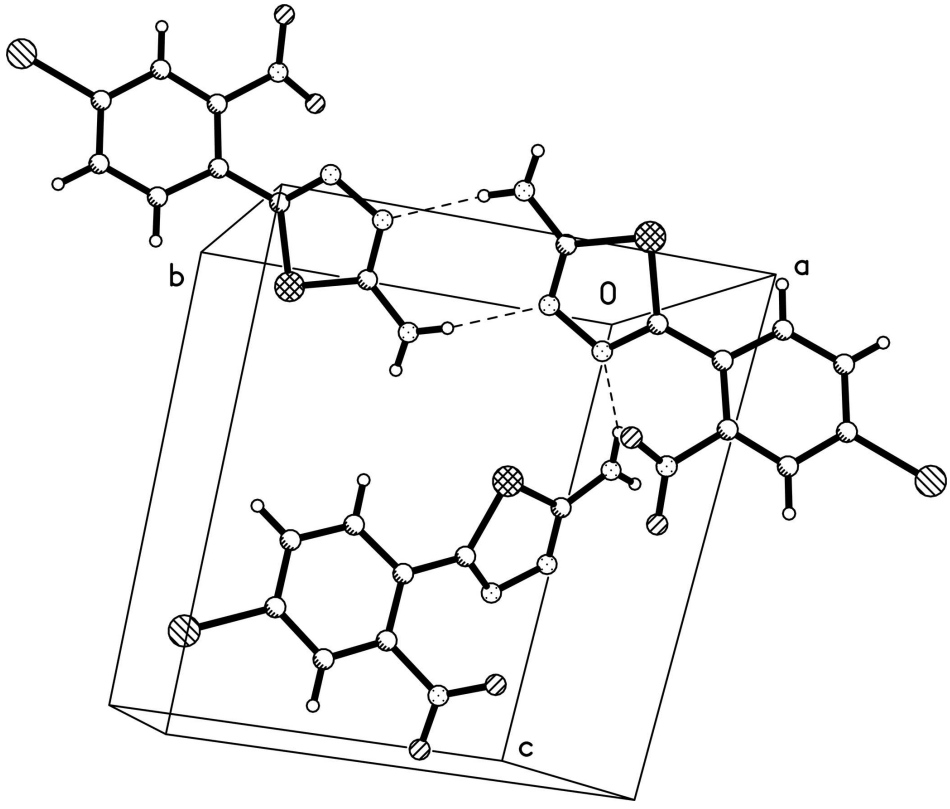

Figure 2

Partial packing view showing the hydrogen bonds network. Dashed lines indicate intermolecular N—H···N hydrogen bonds.

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Crystal data

$C_8H_5BrN_4O_2S$
$M_r = 301.13$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 11.231$ (2) Å
$b = 9.2580$ (19) Å
$c = 10.868$ (2) Å
$\beta = 113.08$ (3)°
$V = 1039.6$ (4) Å^3
$Z = 4$
$F(000) = 592$
$D_x = 1.924$ Mg m^{-3}
Melting point: 506 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–13°
$\mu = 4.14$ mm^{-1}
$T = 293$ K
Block, yellow
0.20 × 0.10 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.491$, $T_{max} = 0.682$
3909 measured reflections
1920 independent reflections
1409 reflections with $I > 2\sigma(I)$
$R_{int} = 0.116$
$\theta_{max} = 25.4°$, $\theta_{min} = 2.0°$
$h = -13\rightarrow12$
$k = -11\rightarrow11$
$l = 0\rightarrow13$
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.104$
$S = 1.01$
1920 reflections
152 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.025P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.97$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0114 (8)

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br	0.11486 (5)	0.01063 (5)	0.19612 (6)	0.0512 (2)
S	0.34305 (13)	0.66328 (12)	0.58298 (11)	0.0389 (3)
C1	0.2933 (5)	0.3456 (5)	0.4493 (4)	0.0398 (11)
H1A	0.3437	0.3551	0.5402	0.048*
N1	0.1367 (4)	0.5710 (4)	0.1441 (4)	0.0370 (9)
O1	0.1374 (4)	0.5588 (4)	0.0330 (3)	0.0585 (10)
O2	0.0937 (3)	0.6740 (3)	0.1818 (3)	0.0517 (10)
N2	0.3728 (4)	0.6948 (4)	0.3620 (3)	0.0357 (9)
C2	0.2492 (5)	0.2112 (5)	0.3991 (5)	0.0418 (12)
H2B	0.2717	0.1308	0.4549	0.050*

N3	0.4262 (4)	0.8176 (4)	0.4373 (3)	0.0339 (9)
C3	0.1724 (4)	0.1958 (4)	0.2670 (5)	0.0360 (10)
C4	0.1413 (5)	0.3137 (5)	0.1816 (4)	0.0339 (11)
H4A	0.0920	0.3029	0.0907	0.041*
N4	0.4674 (5)	0.9189 (5)	0.6472 (4)	0.0460 (12)
H4B	0.486 (6)	0.996 (7)	0.630 (6)	0.055*
H4C	0.446 (5)	0.910 (6)	0.709 (6)	0.055*
C5	0.1853 (4)	0.4459 (5)	0.2350 (4)	0.0331 (10)
C6	0.2654 (4)	0.4671 (4)	0.3696 (4)	0.0283 (9)
C7	0.3245 (4)	0.6062 (5)	0.4235 (4)	0.0303 (9)
C8	0.4186 (4)	0.8148 (4)	0.5534 (4)	0.0318 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.0612 (3)	0.0292 (3)	0.0646 (4)	−0.0078 (3)	0.0262 (3)	−0.0142 (2)
S	0.0593 (7)	0.0333 (6)	0.0300 (5)	−0.0143 (6)	0.0240 (5)	−0.0042 (5)
C1	0.045 (3)	0.037 (2)	0.031 (2)	0.001 (2)	0.008 (2)	0.000 (2)
N1	0.037 (2)	0.036 (2)	0.031 (2)	0.001 (2)	0.0059 (17)	0.0040 (17)
O1	0.073 (2)	0.056 (2)	0.0359 (18)	−0.001 (2)	0.0100 (17)	0.0107 (18)
O2	0.060 (2)	0.0277 (16)	0.057 (2)	0.0082 (18)	0.0115 (19)	0.0035 (16)
N2	0.047 (2)	0.0326 (17)	0.0289 (18)	−0.010 (2)	0.0163 (17)	−0.0061 (16)
C2	0.046 (3)	0.026 (2)	0.044 (3)	−0.003 (2)	0.008 (2)	0.005 (2)
N3	0.045 (2)	0.0318 (18)	0.0267 (18)	−0.0118 (19)	0.0163 (17)	−0.0039 (15)
C3	0.034 (2)	0.0213 (18)	0.053 (3)	−0.005 (2)	0.017 (2)	−0.009 (2)
C4	0.039 (3)	0.031 (2)	0.028 (2)	−0.002 (2)	0.0086 (19)	−0.0053 (18)
N4	0.076 (3)	0.036 (2)	0.033 (2)	−0.023 (2)	0.028 (2)	−0.0124 (19)
C5	0.034 (2)	0.0246 (18)	0.035 (2)	−0.001 (2)	0.007 (2)	−0.0030 (19)
C6	0.034 (2)	0.0274 (19)	0.0261 (19)	−0.005 (2)	0.0140 (17)	−0.0026 (17)
C7	0.034 (2)	0.031 (2)	0.028 (2)	−0.004 (2)	0.0140 (19)	−0.0012 (18)
C8	0.035 (2)	0.027 (2)	0.031 (2)	−0.007 (2)	0.0109 (19)	−0.0013 (18)

Geometric parameters (Å, º)

Br—C3	1.887 (4)	C2—C3	1.362 (7)
S—C8	1.734 (4)	C2—H2B	0.9300
S—C7	1.744 (4)	N3—C8	1.297 (5)
C1—C2	1.371 (6)	C3—C4	1.386 (6)
C1—C6	1.379 (6)	C4—C5	1.361 (6)
C1—H1A	0.9300	C4—H4A	0.9300
N1—O2	1.210 (5)	N4—C8	1.353 (6)
N1—O1	1.215 (5)	N4—H4B	0.79 (6)
N1—C5	1.481 (6)	N4—H4C	0.81 (6)
N2—C7	1.303 (5)	C5—C6	1.399 (6)
N2—N3	1.392 (4)	C6—C7	1.462 (6)
C8—S—C7	86.4 (2)	C3—C4—H4A	121.0
C2—C1—C6	122.2 (4)	C8—N4—H4B	122 (4)

C2—C1—H1A	118.9	C8—N4—H4C	113 (4)
C6—C1—H1A	118.9	H4B—N4—H4C	119 (6)
O2—N1—O1	124.7 (4)	C4—C5—C6	123.3 (4)
O2—N1—C5	118.8 (4)	C4—C5—N1	116.2 (3)
O1—N1—C5	116.4 (4)	C6—C5—N1	120.4 (4)
C7—N2—N3	112.4 (3)	C1—C6—C5	115.9 (4)
C3—C2—C1	119.7 (4)	C1—C6—C7	120.7 (3)
C3—C2—H2B	120.2	C5—C6—C7	123.2 (4)
C1—C2—H2B	120.2	N2—C7—C6	124.3 (4)
C8—N3—N2	112.3 (3)	N2—C7—S	114.1 (3)
C2—C3—C4	120.8 (4)	C6—C7—S	121.6 (3)
C2—C3—Br	119.9 (3)	N3—C8—N4	123.8 (4)
C4—C3—Br	119.1 (3)	N3—C8—S	114.8 (3)
C5—C4—C3	118.0 (4)	N4—C8—S	121.3 (3)
C5—C4—H4A	121.0		

C6—C1—C2—C3	−1.8 (8)	N1—C5—C6—C1	172.8 (4)
C7—N2—N3—C8	1.5 (5)	C4—C5—C6—C7	172.7 (5)
C1—C2—C3—C4	2.1 (8)	N1—C5—C6—C7	−11.3 (7)
C1—C2—C3—Br	178.4 (4)	N3—N2—C7—C6	−178.4 (4)
C2—C3—C4—C5	−2.8 (7)	N3—N2—C7—S	−1.3 (5)
Br—C3—C4—C5	−179.2 (4)	C1—C6—C7—N2	135.9 (5)
C3—C4—C5—C6	3.5 (8)	C5—C6—C7—N2	−39.8 (7)
C3—C4—C5—N1	−172.6 (4)	C1—C6—C7—S	−40.9 (6)
O2—N1—C5—C4	130.8 (5)	C5—C6—C7—S	143.4 (4)
O1—N1—C5—C4	−45.7 (6)	C8—S—C7—N2	0.7 (4)
O2—N1—C5—C6	−45.5 (6)	C8—S—C7—C6	177.8 (4)
O1—N1—C5—C6	138.1 (5)	N2—N3—C8—N4	177.6 (4)
C2—C1—C6—C5	2.3 (7)	N2—N3—C8—S	−1.0 (5)
C2—C1—C6—C7	−173.7 (5)	C7—S—C8—N3	0.2 (4)
C4—C5—C6—C1	−3.1 (7)	C7—S—C8—N4	−178.4 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*B*···N3^{i}	0.79 (7)	2.25 (7)	3.014 (6)	165 (7)
N4—H4*C*···N2^{ii}	0.80 (6)	2.34 (6)	3.103 (6)	161 (6)

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