organic compounds

6-Iodo-2-methyl-1,3-benzothiazole

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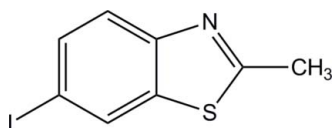Correspondence e-mail: mdjakovic@chem.pmf.hr

The title compound, C_8H_6INS, is essentially planar, the largest deviation from the mean plane being for the I atom [0.075 (3) Å]. The crystal structure is mainly stabilized by intermolecular C—I⋯N halogen bonds, forming zigzag supramolecular chains in [10$\bar{1}$]. Relatively short off-set π–π contacts [centroid–centroid distance = 3.758 (2) Å] between the thiazole rings of inversion-related molecules link neighbouring chains and provide the secondary interactions for building the crystal structure.

Related literature

For the application of benzothiazoles as biologically active compounds, see: Leong *et al.* (2004); Yildiz-Oren *et al.* (2004); Lockhart *et al.* (2005); Sheng *et al.* (2007). For the synthesis of the title compound, see: Racané *et al.* (2006, 2011). For related 1,3-benzothiazole structures, see: Matković-Čalogović *et al.* (2003); Pavlović *et al.* (2009); Đaković *et al.* (2009); Čičak *et al.* (2010). For graph-set theory, see: Etter (1990); Bernstein *et al.* (1995). For a description of the Cambridge Structural Database, see: Allen (2002).

Experimental

Crystal data

C_8H_6INS	V = 884.76 (6) Å^3
M_r = 275.11	Z = 4
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
a = 8.3255 (3) Å	μ = 3.79 mm^{-1}
b = 7.6967 (3) Å	T = 296 K
c = 13.8083 (5) Å	0.47 × 0.38 × 0.14 mm
β = 90.686 (4)°	

Data collection

Oxford Diffraction Xcalibur diffractometer with a Saphire-3 CCD detector	Diffraction, 2009)
	T_{min} = 0.253, T_{max} = 0.658
	13190 measured reflections
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford	1928 independent reflections
	1729 reflections with $I > 2\sigma(I)$
	R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024	101 parameters
$wR(F^2)$ = 0.064	H-atom parameters constrained
S = 1.06	$\Delta\rho_{max}$ = 0.84 e Å^{-3}
1928 reflections	$\Delta\rho_{min}$ = −0.72 e Å^{-3}

Table 1
Halogen-bond geometry (Å, °).

	C4—I1	I1⋯N1^i	C4⋯N1^i	C4—I1⋯N1^i
C4—I1⋯N1^i	2.103 (3)	3.158 (2)	5.257 (4)	175.99 (9)

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; 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: *SHELXL97* and *PLATON* (Spek, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2389).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bernstein, J., Davies, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Čičak, H., Đaković, M., Mihalić, Z., Pavlović, G., Racané, L. & Tralić-Kulenović, V. (2010). *J. Mol. Struct.* **975**, 115–127.
Đaković, M., Čičak, H., Soldin, Ž. & Tralić-Kulenović, V. (2009). *J. Mol. Struct.* **938**, 125–132.
Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Leong, C. O., Suggitt, M., Swaine, D. J., Bibby, M. C., Stevens, M. F. G. & Bradshaw, T. D. (2004). *Mol. Cancer Ther.* **3**, 1565–1575.
Lockhart, A., Ye, L., Judd, D. B., Merritt, A. T., Lowe, P. N., Morgenstern, J. L., Hong, G., Gee, A. D. & Brown, J. (2005). *J. Biol. Chem.* **280**, 7677–7684.
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.
Matković-Čalogović, D., Popović, Z., Tralić-Kulenović, V., Racanè, L. & Karminski-Zamola, G. (2003). *Acta Cryst.* C**59**, o190–o191.
Oxford Diffraction (2009). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.
Pavlović, G., Racané, L. & Čičak, H. (2009). *Dyes Pigments*, **83**, 354–362.
Racané, L., Čičak, H., Mihalić, Z., Karminski-Zamola, G. & Tralić-Kulenović, V. (2011). *Tetrahedron Lett.* In the press.
Racané, L., Tralić-Kulenović, V., Pavlović, G. & Karminski-Zamola, G. (2006). *Heterocycles*, **68**, 1909–1916.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheng, C., Zhu, J., Zhang, W., Zhang, M., Ji, H., Song, Y., Xu, H., Yao, J., Miao, Z., Zhou, Y., Zhu, J. & Lü, J. (2007). *Eur. J. Med. Chem.* **42**, 477–486.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Yildiz-Oren, I., Yalcin, I., Aki-Sener, E. & Ucarturk, N. (2004). *Eur. J. Med. Chem.* **39**, 291–298.

supporting information

6-Iodo-2-methyl-1,3-benzothiazole

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S1. Comment

This work was a part of our preparative, structural, mechanistic and computational investigation of a series of substituted benzothiazoles (bta), which attract considerable interest due to their biological activities.

The molecule is almost ideally planar (r.m.s. deviation = 0.009 Å), with the largest deviation from the plane being that of atom I1 [0.075 (3) Å] (Fig.1). The geometry of the benzothiazole rings is consistent with other 1,3-benzothiazoles listed in the CSD base (Allen *et al.*, 2002). The two S—C bonds of the thiazole ring [S1—C1 and S1—C2] differ with respect to each other, but both are within two bortherline cases, single S—C [1.82 Å] and double S=C [1.56 Å], while the endocyclic C—N bond is dominantly double in character. The differences in C—C bonds within benzene ring are common for such fused rings.

In the crystal structure halogen bonds are the principal specific interactions responsible for the crystal packing. There is only one short and directional C—I···N contact [C—I = 2.103 (3) Å] (see Table 1) that link the molecules into antiparallel zigzag C(7) chains (Etter, 1990; Bernstein *et al.*, 1995) in [1 0 - 1] direction (Figs. 2 and 3).

Relatively short off-set π–π contacts [Cg···Cg = 3.758 (2) Å] between the thiazole rings, belonging to the molecules that are related by an inversion centre, link the neighboring supramolecular chains and provide the secondary interactions for building the crystal structure.

The structure of the title compound is one more example showing that halogen bonding is also as effective and reliable tool for assembling molecules into supramolecular architectures.

S2. Experimental

Colourless single crystals of the title compound were obtained by slow evaporation of a dichloromethane solution.

S3. Refinement

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent C atom at distances of 0.93 or 0.96 Å for aromatic or methyl H atoms, respectively, and with U_{iso}(H) = $1.2U_{eq}$(C) (for aromatic H) or U_{iso}(H) = $1.5U_{eq}$(C) (for methyl group).
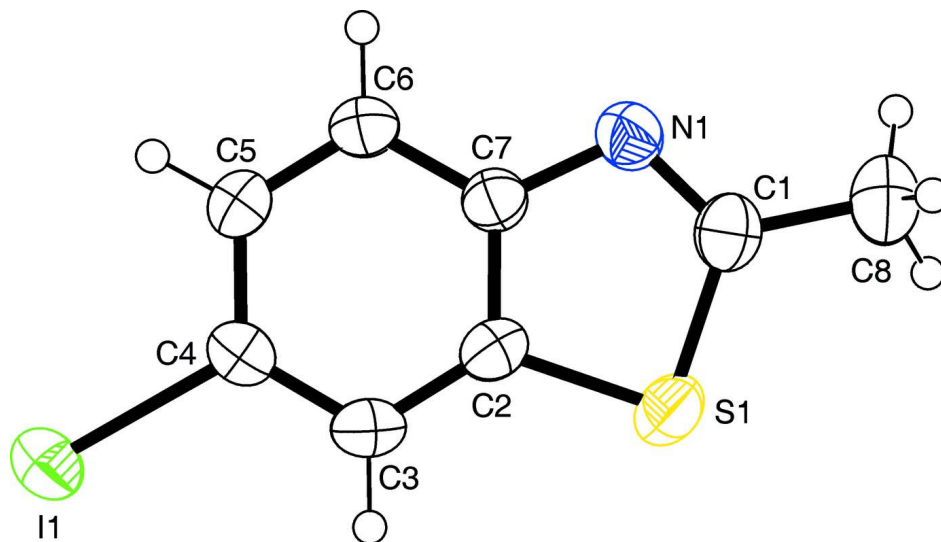
Figure 1

Molecular structure of the title compound with the atom labeling scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.
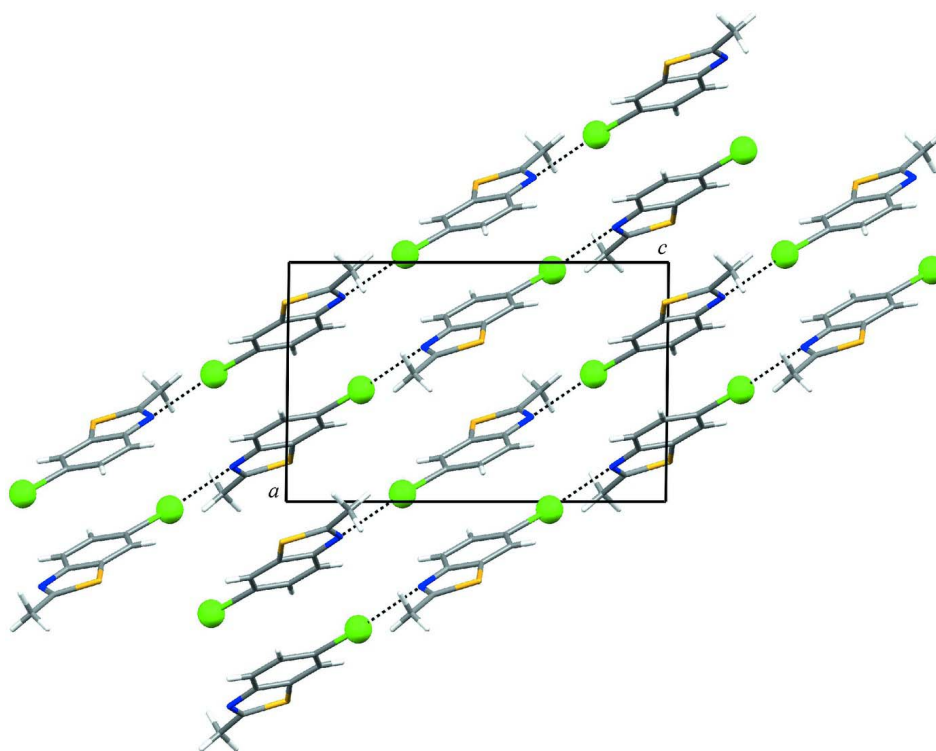
Figure 2

Crystal packing of the title compound viewed down the *b* axis showing halogen bonds as dashed lines.
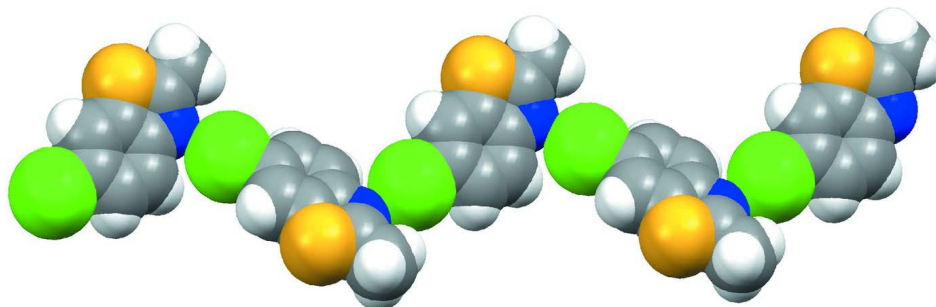
Figure 3

Spacefill representaton of a zigzag halogen bonding chain running in [1 0 - 1].

6-Iodo-2-methyl-1,3-benzothiazole

Crystal data

C_8H_6INS	$F(000) = 520$
$M_r = 275.11$	$D_x = 2.065$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 10010 reflections
$a = 8.3255$ (3) Å	$\theta = 4.4$–32.6°
$b = 7.6967$ (3) Å	$\mu = 3.79$ mm^{-1}
$c = 13.8083$ (5) Å	$T = 296$ K
$\beta = 90.686$ (4)°	Plate, colourless
$V = 884.76$ (6) Å^3	$0.47 \times 0.38 \times 0.14$ mm
$Z = 4$	

Data collection

Oxford Diffraction Xcalibur diffractometer with a Saphire-3 CCD detector	13190 measured reflections
	1928 independent reflections
Radiation source: Enhance (Mo) X-ray Source	1729 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.027$
Detector resolution: 16.3426 pixels mm^{-1}	$\theta_{max} = 27.0°$, $\theta_{min} = 4.6°$
CCD scans	$h = -10 \rightarrow 10$
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)	$k = -9 \rightarrow 9$
	$l = -17 \rightarrow 17$
$T_{min} = 0.253$, $T_{max} = 0.658$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.024$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.064$	
$S = 1.06$	H-atom parameters constrained
1928 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.4162P]$ where $P = (F_o^2 + 2F_c^2)/3$
101 parameters	
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.84$ e Å^{-3}
	$\Delta\rho_{min} = -0.72$ e Å^{-3}

Special details

Experimental. Solvent used: CH_2Cl_2 Crystal mount: glued on a glass fibre Mosaicity (°): 1.1 (1) Frames collected: 892 Seconds exposure per frame: 5 Degree rotation per frame: 1.0 Crystal-Detector distance (mm): 50.0.

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses 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 observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -R-factor-obs *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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.96733 (2)	0.14994 (3)	0.30624 (1)	0.0485 (1)
S1	0.66879 (11)	0.75187 (9)	0.49021 (6)	0.0518 (3)
N1	0.6453 (3)	0.5615 (3)	0.64355 (18)	0.0447 (8)
C1	0.6117 (4)	0.7135 (4)	0.6097 (2)	0.0457 (9)
C2	0.7440 (3)	0.5425 (3)	0.4842 (2)	0.0392 (8)
C3	0.8155 (3)	0.4585 (4)	0.40718 (19)	0.0430 (8)
C4	0.8633 (3)	0.2887 (4)	0.42068 (19)	0.0399 (8)
C5	0.8427 (4)	0.2058 (4)	0.5097 (2)	0.0452 (9)
C6	0.7728 (4)	0.2900 (4)	0.5857 (2)	0.0467 (9)
C7	0.7211 (3)	0.4614 (3)	0.5734 (2)	0.0386 (7)
C8	0.5343 (5)	0.8546 (4)	0.6669 (3)	0.0600 (11)
H3	0.83070	0.51470	0.34840	0.0520*
H5	0.87710	0.09160	0.51740	0.0540*
H6	0.75980	0.23380	0.64480	0.0560*
H8A	0.46780	0.80420	0.71580	0.0900*
H8B	0.46950	0.92540	0.62460	0.0900*
H8C	0.61580	0.92510	0.69710	0.0900*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0488 (1)	0.0567 (2)	0.0402 (1)	0.0012 (1)	0.0048 (1)	−0.0055 (1)
S1	0.0658 (5)	0.0376 (4)	0.0518 (4)	0.0063 (3)	−0.0035 (3)	0.0058 (3)
N1	0.0487 (13)	0.0419 (13)	0.0437 (13)	−0.0022 (10)	0.0082 (10)	−0.0014 (10)
C1	0.0416 (14)	0.0411 (14)	0.0543 (17)	−0.0019 (12)	−0.0027 (12)	−0.0054 (12)
C2	0.0424 (14)	0.0345 (12)	0.0407 (13)	−0.0029 (11)	−0.0035 (11)	0.0049 (11)
C3	0.0482 (15)	0.0457 (14)	0.0351 (13)	−0.0040 (12)	−0.0001 (11)	0.0075 (12)
C4	0.0393 (14)	0.0457 (14)	0.0347 (13)	−0.0025 (11)	0.0025 (11)	−0.0027 (11)
C5	0.0536 (16)	0.0347 (13)	0.0474 (16)	0.0044 (12)	0.0043 (13)	0.0030 (11)
C6	0.0593 (18)	0.0394 (13)	0.0415 (15)	−0.0005 (13)	0.0114 (13)	0.0073 (12)
C7	0.0396 (13)	0.0364 (12)	0.0399 (13)	−0.0035 (11)	0.0037 (10)	0.0013 (10)
C8	0.062 (2)	0.0511 (19)	0.067 (2)	0.0089 (15)	−0.0004 (17)	−0.0108 (15)

Geometric parameters (Å, º)

I1—C4	2.103 (3)	C4—C5	1.397 (4)
S1—C1	1.748 (3)	C5—C6	1.369 (4)
S1—C2	1.731 (2)	C6—C7	1.397 (4)
N1—C1	1.289 (4)	C3—H3	0.9300
N1—C7	1.395 (4)	C5—H5	0.9300
C1—C8	1.494 (5)	C6—H6	0.9300
C2—C3	1.385 (4)	C8—H8A	0.9600
C2—C7	1.396 (4)	C8—H8B	0.9600
C3—C4	1.378 (4)	C8—H8C	0.9600
I1···C1[i]	3.826 (3)	H3···H8A[vii]	2.5800
I1···N1[ii]	3.158 (2)	H5···S1[viii]	3.1600
I1···H5[iii]	3.3100	H5···I1[iii]	3.3100
S1···H5[iv]	3.1600	H5···H5[iii]	2.5400
S1···H8B[v]	3.1600	H8A···H3[ix]	2.5800
N1···I1[vi]	3.158 (2)	H8B···S1[v]	3.1600
C1···I1[i]	3.826 (3)		
C1—S1—C2	89.46 (14)	N1—C7—C6	125.3 (2)
C1—N1—C7	110.3 (2)	C2—C7—C6	119.0 (2)
S1—C1—N1	115.8 (2)	C2—C3—H3	121.00
S1—C1—C8	120.0 (2)	C4—C3—H3	121.00
N1—C1—C8	124.1 (3)	C4—C5—H5	119.00
S1—C2—C3	129.1 (2)	C6—C5—H5	120.00
S1—C2—C7	108.70 (19)	C5—C6—H6	120.00
C3—C2—C7	122.2 (2)	C7—C6—H6	120.00
C2—C3—C4	117.7 (2)	C1—C8—H8A	110.00
I1—C4—C3	120.06 (19)	C1—C8—H8B	110.00
I1—C4—C5	119.0 (2)	C1—C8—H8C	109.00
C3—C4—C5	120.9 (3)	H8A—C8—H8B	109.00
C4—C5—C6	121.1 (3)	H8A—C8—H8C	109.00
C5—C6—C7	119.1 (3)	H8B—C8—H8C	109.00
N1—C7—C2	115.7 (2)		
C2—S1—C1—N1	0.5 (3)	S1—C2—C7—C6	180.0 (2)
C2—S1—C1—C8	178.5 (3)	C3—C2—C7—N1	−179.1 (2)
C1—S1—C2—C3	179.0 (3)	C3—C2—C7—C6	0.4 (4)
C1—S1—C2—C7	−0.6 (2)	C2—C3—C4—I1	178.41 (19)
C7—N1—C1—S1	−0.3 (3)	C2—C3—C4—C5	−1.1 (4)
C7—N1—C1—C8	−178.2 (3)	I1—C4—C5—C6	−178.8 (2)
C1—N1—C7—C2	−0.2 (3)	C3—C4—C5—C6	0.8 (5)
C1—N1—C7—C6	−179.6 (3)	C4—C5—C6—C7	0.2 (5)
S1—C2—C3—C4	−179.0 (2)	C5—C6—C7—N1	178.6 (3)

| C7—C2—C3—C4 | 0.6 (4) | C5—C6—C7—C2 | −0.8 (4) |
| S1—C2—C7—N1 | 0.5 (3) | | |

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) *x*+1/2, −*y*+1/2, *z*−1/2; (iii) −*x*+2, −*y*, −*z*+1; (iv) *x*, *y*+1, *z*; (v) −*x*+1, −*y*+2, −*z*+1; (vi) *x*−1/2, −*y*+1/2, *z*+1/2; (vii) *x*+1/2, −*y*+3/2, *z*−1/2; (viii) *x*, *y*−1, *z*; (ix) *x*−1/2, −*y*+3/2, *z*+1/2.