Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(*Z*)-*N*-{3-[(2-Chloro-1,3-thiazol-5-yl)-methyl]-1,3-thiazolidin-2-ylidene}-cyanamide

Yue-Ming Li,[a] Jian-Ye Li,[b] Qian Wang,[c] Ai-You Hao[a]* and Tao Sun[a]

[a]School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, People's Republic of China, [b]Chemical Engineering Department, Weifang University of Science and Technology, Shouguang 262700, People's Republic of China, and [c]Beijing University of Chemical Technology, Beijing 100029, People's Republic of China
Correspondence e-mail: haoay@sdu.edu.cn

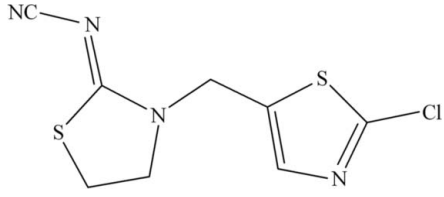
Received 18 October 2011; accepted 9 November 2011

Key indicators: single-crystal X-ray study; T = 273 K; mean σ(C–C) = 0.003 Å; R factor = 0.033; wR factor = 0.108; data-to-parameter ratio = 17.9.

In the title compound, $C_8H_7ClN_4S_2$, the thiazole ring is essentially planar [r.m.s. deviation = 0.0011 (2) Å] and conformation of the thiazolidine ring is twisted on the C—C bond. The C=N bond has a Z configuration.

Related literature

The title compound was synthesized as an intermediate for the preparation of pesticides. For the biological activity of this class of compounds, see: Zhang *et al.* (2000); Kagabu *et al.* (2008). For the synthesis, see: Kozo *et al.* (1987); Zuo *et al.* (2008). For a related structure. see Li *et al.* (2010).



Experimental

Crystal data

$C_8H_7ClN_4S_2$
M_r = 258.75
Monoclinic, $P2_1/n$
a = 9.6331 (12) Å
b = 11.2657 (14) Å
c = 10.7675 (13) Å
β = 112.433 (2)°
V = 1080.1 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.71 mm^{-1}
T = 273 K
0.15 × 0.10 × 0.10 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.901, T_{max} = 0.932
6191 measured reflections
2440 independent reflections
2075 reflections with $I > 2\sigma(I)$
R_{int} = 0.015

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.108
S = 0.98
2440 reflections
136 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; 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*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5358).

References

Bruker (1998). *SMART* and *SAINT*, Bruker AXS Inc., Madison, Wisconsin, USA.
Kagabu, S., Nishimura, K., Naruse, Y. & Ohno, I. (2008). *J. Pestic. Sci.* **33**, 58–66.
Kozo, S., Shinichi, T., Shinzo, K., Shoko, S., Koichi, M. & Yumi, H. (1987). EP Patent 235725.
Li, H., Zhang, X. & Xu, L. (2010). *Acta Cryst.* E**66**, o2171.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Zhang, A. G., Kayser, H., Maiensch, P. & Casida, J. E. (2000). *J. Neurochem.* **75**, 1294–1303.
Zuo, B. J., Shi, L. P., Li, L., Li, X. K. & Zhuang, Z. X. (2008). CN Patent 101250165.

supporting information

Acta Cryst. (2011). E**67**, o3303 [https://doi.org/10.1107/S1600536811047404]

(*Z*)-*N*-{3-[(2-Chloro-1,3-thiazol-5-yl)methyl]-1,3-thiazolidin-2-ylidene}cyanamide

Yue-Ming Li, Jian-Ye Li, Qian Wang, Ai-You Hao and Tao Sun

S1. Comment

It is already known that certain cyanoimino-subsitituted heterocyclic compounds are useful as intermediates in the preparation of pesticides which have played a major role in eliminating insects such as aphids, leafhoppers and whiteflies (Kagabu *et al.*, 2008; Zhang *et al.*, 2000). The molecular structure of the title compound is shown in Fig. 1. The thiazole ring is essentially planar (r.m.s. deviations 0.0011 (2)Å) and the thiazolidine ring is is in a slight half-chair conformation. The C═N bond with a *Z* configuration has a bond length of 1.150 (4) Å, which is in agreement with that in a related structure (Li *et al.*, 2010).

S2. Experimental

The synthesis of the title compound follows the method of Kozo *et al.* (1987) and Zuo, *et al.* (2008). (*Z*)-2-(1,3-Thiazolidin-2-ylidene)cyanamide 12.7 g (0.1 mol) and potassium carbonate 41.4 g (0.3 mol) were dissolved in *N*,*N*-dimethylformamide (DMF) (75 ml), then 2-chloro-5-thiazolylmethyl chloride 17.4 g (0.102 mol) dissolved in DMF (40 ml) was added dropwise. The mixture was stirred for 0.5 h at room temperature and filtered. The filtrate was concentrated and further purified by column chromatography to obtain the title product (13.9 g) with a yield of 53.7% Colorless crystals were obtained by slow evaporation of a tetrahydrofuran solution of the title compound at room temperature.

^{1}H NMR (300 MHz, DMSO-d6): δ (p.p.m.) 7.71 (1*H*, s), 4.79 (2*H*, s), 3.92 (2*H*, t, *J* = 15.3 Hz, *J* = 7.65 Hz); 3.49 (2*H*, t, *J* = 15.3 Hz, *J* = 7.65 Hz).

S3. Refinement

All H atoms were placed in calculated positions, with C—H = 0.93-0.97 Å and included in the final cycles of refinement using a riding model, with *U*iso(H) = 1.2*U*eq(C).

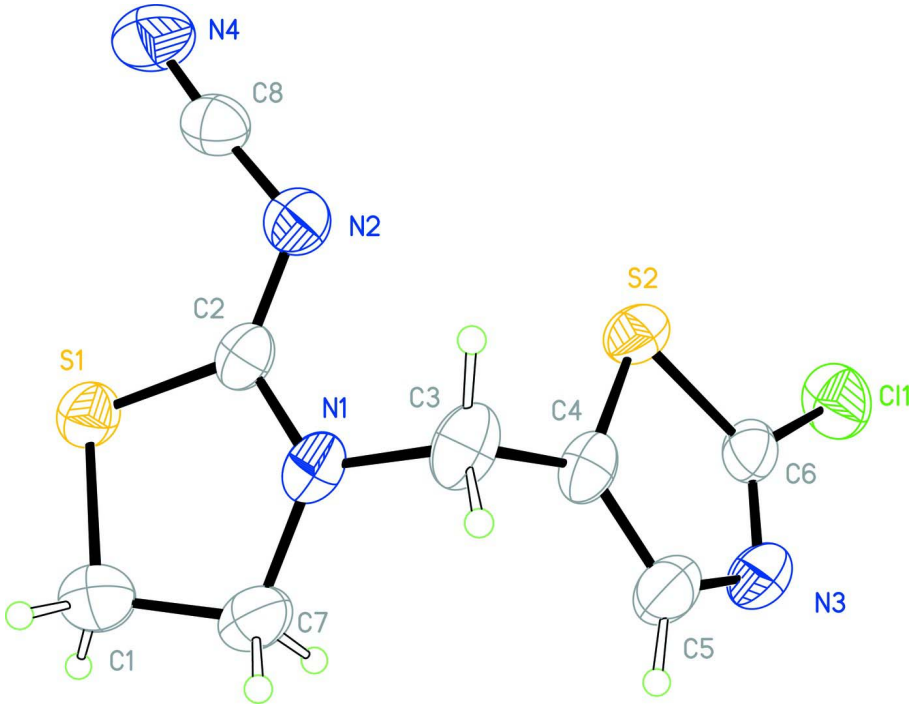


Figure 1

The molecular structure of the title compound showing displacement ellipsoids at the 40% probability level.

(*Z*)-*N*-{3-[(2-Chloro-1,3-thiazol-5-yl)methyl]-1,3-thiazolidin-2- ylidene}cyanamide

Crystal data

$C_8H_7ClN_4S_2$
$M_r = 258.75$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 9.6331$ (12) Å
$b = 11.2657$ (14) Å
$c = 10.7675$ (13) Å
$\beta = 112.433$ (2)°
$V = 1080.1$ (2) Å^3
$Z = 4$
$F(000) = 528$
$D_x = 1.591$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3349 reflections
$\theta = 2.7$–27.5°
$\mu = 0.71$ mm^{-1}
$T = 273$ K
Block, colorless
0.15 × 0.10 × 0.10 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.901$, $T_{max} = 0.932$
6191 measured reflections
2440 independent reflections
2075 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.4°$
$h = -12 \rightarrow 12$
$k = -11 \rightarrow 14$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.108$
$S = 0.98$
2440 reflections
136 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
$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 0.5077P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.22859 (6)	0.11411 (5)	0.45559 (5)	0.04850 (16)
S2	0.42112 (6)	0.16077 (5)	0.07049 (5)	0.04881 (17)
Cl1	0.30959 (8)	0.27500 (7)	−0.19805 (6)	0.0715 (2)
N1	0.3166 (2)	−0.00659 (14)	0.29672 (16)	0.0445 (4)
C4	0.3566 (2)	0.02118 (18)	0.08619 (19)	0.0452 (4)
C2	0.3576 (2)	0.08458 (16)	0.38105 (18)	0.0398 (4)
C3	0.4033 (3)	−0.0430 (2)	0.2174 (2)	0.0532 (5)
H3A	0.3906	−0.1277	0.2004	0.064*
H3B	0.5090	−0.0282	0.2688	0.064*
C1	0.1211 (3)	−0.0170 (2)	0.3809 (3)	0.0680 (7)
H1A	0.1433	−0.0804	0.4466	0.082*
H1B	0.0144	0.0000	0.3481	0.082*
N2	0.4818 (2)	0.14397 (16)	0.40261 (18)	0.0485 (4)
C6	0.3112 (2)	0.1563 (2)	−0.09762 (19)	0.0475 (5)
N3	0.2328 (2)	0.0626 (2)	−0.14132 (17)	0.0598 (5)
C8	0.5191 (2)	0.22657 (19)	0.4975 (2)	0.0484 (5)
N4	0.5597 (3)	0.29942 (19)	0.5786 (2)	0.0680 (6)
C7	0.1657 (3)	−0.05279 (19)	0.2663 (2)	0.0527 (5)
H7A	0.1649	−0.1385	0.2579	0.063*
H7B	0.0961	−0.0197	0.1824	0.063*
C5	0.2592 (3)	−0.0145 (2)	−0.0353 (2)	0.0580 (6)
H5A	0.2118	−0.0880	−0.0471	0.070*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0521 (3)	0.0483 (3)	0.0467 (3)	0.0000 (2)	0.0207 (2)	−0.0068 (2)
S2	0.0445 (3)	0.0554 (3)	0.0384 (3)	−0.0010 (2)	0.0067 (2)	−0.0027 (2)
Cl1	0.0720 (4)	0.0877 (5)	0.0533 (3)	0.0002 (3)	0.0224 (3)	0.0209 (3)
N1	0.0568 (10)	0.0397 (8)	0.0339 (7)	0.0054 (7)	0.0139 (7)	−0.0003 (6)
C4	0.0520 (11)	0.0470 (10)	0.0371 (9)	0.0097 (8)	0.0176 (8)	−0.0041 (8)
C2	0.0474 (10)	0.0364 (9)	0.0315 (8)	0.0081 (7)	0.0104 (7)	0.0059 (7)
C3	0.0686 (14)	0.0465 (11)	0.0433 (10)	0.0187 (10)	0.0200 (10)	0.0000 (9)
C1	0.0731 (16)	0.0668 (15)	0.0673 (15)	−0.0213 (13)	0.0304 (13)	−0.0164 (12)
N2	0.0487 (9)	0.0484 (9)	0.0476 (9)	0.0013 (7)	0.0174 (8)	0.0004 (8)
C6	0.0418 (10)	0.0644 (13)	0.0353 (9)	0.0028 (9)	0.0137 (8)	0.0014 (9)
N3	0.0615 (11)	0.0772 (13)	0.0347 (8)	−0.0110 (10)	0.0114 (8)	−0.0067 (9)
C8	0.0432 (10)	0.0453 (11)	0.0526 (11)	−0.0015 (8)	0.0139 (9)	0.0059 (9)
N4	0.0686 (13)	0.0557 (12)	0.0721 (13)	−0.0149 (10)	0.0185 (11)	−0.0115 (10)
C7	0.0626 (13)	0.0431 (10)	0.0436 (10)	−0.0065 (9)	0.0105 (9)	−0.0029 (9)
C5	0.0721 (14)	0.0561 (13)	0.0446 (11)	−0.0100 (11)	0.0210 (10)	−0.0122 (10)

Geometric parameters (Å, º)

S1—C2	1.749 (2)	C3—H3B	0.9700
S1—C1	1.807 (2)	C1—C7	1.508 (3)
S2—C6	1.714 (2)	C1—H1A	0.9700
S2—C4	1.723 (2)	C1—H1B	0.9700
Cl1—C6	1.716 (2)	N2—C8	1.326 (3)
N1—C2	1.327 (2)	C6—N3	1.279 (3)
N1—C7	1.459 (3)	N3—C5	1.378 (3)
N1—C3	1.463 (3)	C8—N4	1.153 (3)
C4—C5	1.348 (3)	C7—H7A	0.9700
C4—C3	1.495 (3)	C7—H7B	0.9700
C2—N2	1.313 (3)	C5—H5A	0.9300
C3—H3A	0.9700		
C2—S1—C1	91.54 (11)	S1—C1—H1A	110.4
C6—S2—C4	88.65 (10)	C7—C1—H1B	110.4
C2—N1—C7	116.13 (17)	S1—C1—H1B	110.4
C2—N1—C3	121.99 (18)	H1A—C1—H1B	108.6
C7—N1—C3	120.70 (17)	C2—N2—C8	117.03 (18)
C5—C4—C3	128.3 (2)	N3—C6—S2	116.92 (17)
C5—C4—S2	108.70 (17)	N3—C6—Cl1	123.34 (16)
C3—C4—S2	123.00 (16)	S2—C6—Cl1	119.75 (13)
N2—C2—N1	121.90 (18)	C6—N3—C5	108.62 (18)
N2—C2—S1	125.56 (15)	N4—C8—N2	175.7 (2)
N1—C2—S1	112.54 (15)	N1—C7—C1	106.93 (17)
N1—C3—C4	112.53 (17)	N1—C7—H7A	110.3
N1—C3—H3A	109.1	C1—C7—H7A	110.3
C4—C3—H3A	109.1	N1—C7—H7B	110.3

N1—C3—H3B	109.1	C1—C7—H7B	110.3
C4—C3—H3B	109.1	H7A—C7—H7B	108.6
H3A—C3—H3B	107.8	C4—C5—N3	117.1 (2)
C7—C1—S1	106.81 (17)	C4—C5—H5A	121.4
C7—C1—H1A	110.4	N3—C5—H5A	121.4
C6—S2—C4—C5	−0.26 (17)	N1—C2—N2—C8	−174.14 (18)
C6—S2—C4—C3	−178.81 (18)	S1—C2—N2—C8	6.2 (3)
C7—N1—C2—N2	−170.80 (17)	C4—S2—C6—N3	0.15 (19)
C3—N1—C2—N2	−3.1 (3)	C4—S2—C6—Cl1	179.78 (14)
C7—N1—C2—S1	8.9 (2)	S2—C6—N3—C5	0.0 (3)
C3—N1—C2—S1	176.56 (14)	Cl1—C6—N3—C5	−179.61 (17)
C1—S1—C2—N2	−174.02 (19)	C2—N1—C7—C1	−22.8 (2)
C1—S1—C2—N1	6.31 (16)	C3—N1—C7—C1	169.36 (19)
C2—N1—C3—C4	−88.0 (2)	S1—C1—C7—N1	25.2 (2)
C7—N1—C3—C4	79.1 (2)	C3—C4—C5—N3	178.8 (2)
C5—C4—C3—N1	−95.7 (3)	S2—C4—C5—N3	0.3 (3)
S2—C4—C3—N1	82.6 (2)	C6—N3—C5—C4	−0.2 (3)
C2—S1—C1—C7	−18.40 (19)		