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1-(2-Chloro-1,3-thiazol-5-ylmethyl)-3,5-dimethyl-2-nitrimino-1,2,3,4,5,6-hexahydro-1,3,5-triazine

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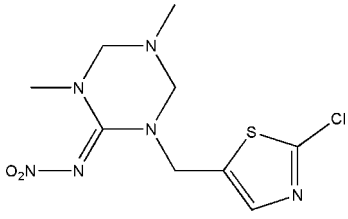
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.049; wR factor = 0.145; data-to-parameter ratio = 13.7.

In the title compound, $C_9H_{13}ClN_6O_2S$, all bond lengths and angles are normal. The 1,3,5-triazine ring exhibits a half-chair conformation. In the crystal structure, weak intermolecular C—H···N and C—H···O hydrogen bonds link the molecules into layers parallel to the *bc* plane.

Related literature

For synthesis of the title compound, see: Frank *et al.* (1990). For related crystal structures, see: Zurn *et al.* (1982). For useful applications of related compounds, see: Motohiro (2000).



Experimental

Crystal data

$C_9H_{13}ClN_6O_2S$
M_r = 304.76
Monoclinic, $C2/c$
a = 32.864 (7) Å
b = 6.4063 (13) Å
c = 13.569 (3) Å
β = 110.53 (3)°
V = 2675.3 (11) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.45 mm^{-1}
T = 293 (2) K
0.32 × 0.22 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID IP area-detector diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi 1995)
T_{min} = 0.869, T_{max} = 0.956
9419 measured reflections
2363 independent reflections
1985 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.145
S = 1.17
2363 reflections
173 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4A···N3^{i}	0.97	2.45	3.314 (3)	148
C4—H4B···O1^{ii}	0.97	2.36	3.178 (3)	142
C7—H7A···O2^{iii}	0.97	2.58	3.483 (4)	156

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

Data collection: *RAPID-AUTO* (Rigaku 2004); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2360).

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supplementary materials

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1-(2-Chloro-1,3-thiazol-5-ylmethyl)-3,5-dimethyl-2-nitrimino-1,2,3,4,5,6-hexahydro-1,3,5-triazine

Z.-Q. Hu, X.-D. Yang, G.-W. An, Z. Yang and L.-Z. Xu

Comment

Crop protection and veterinary pest control have changed greatly with the recent introduction of neonicotinoid insecticides represented by imidacloprid, the only major new class of chemical insecticides of the last three decades. They are increasingly utilized throughout the world (billion-dollar-a-year market), and seven neonicotinoid insecticide are commercialized or nearly on the market at present and expected to become fourth major insecticide group following the organophosphates, methylcarbamates and pyrethroids (Motohiro, 2000). Clothianidin is a neonicotinoid insecticide that was synthesized in Japan by Takeda Chemical. The title compound (I) was synthesized as an intermediate for the synthesis of clothianidin. We report here the crystal structure of (I).

In (I) (Fig. 1), all bond lengths and angles are normal and in a good agreement with those reported previously (Zurn *et al.*, 1982). The title compound contains three planar fragments, which includes thiazole ring C1—C3/N1/S1 and a triazine ring C5—C7/N2/N3. The triazine ring forms two planes - C5/C6/C7/N2 and N3/C5/C7, respectively, with a dihedral angle of 50.8 (2)° between them. The crystal structure is stabilized by intermolecular C—H···O and N—H···O hydrogen bonds (Table 1, Fig. 2).

Experimental

1,5-Dimethyl-2-nitroiminohexahydro-1,3,5-triazine1.72 g (0.01 mol) was dissolved in 20 ml of dried DMF. To the solution, 60% sodium hydride 0.28 g(0.012 mol) was added portionwise with cooling. The mixture was stirred for 1 h at room temperature until evolution of hydrogen was ceased and then the mixture was heated with strring further for 1 h at 50° C. To the mixture, a solution of 2-chloro-5-thiazolymethylchloride1.72 g (0.01 mol) in 8 ml of dried DMF was added dropwise at 40–50° C. After this additon,the reaction mixture was heated with strring for two hours at 70–80° C. The mixture was poured into ice-water and extracted with dichloromethane. The extract was dried over anhydrous magnesium sulfate, and dichloromethane was distilled off. The residue was purified by a column chromatography to obtain the title compound(0.82 g, yield 27%)·(Frank *et al.*, 1990). Single crystals suitable for X-ray measurement were obtained by recrystallization from dichloromethane at room temperature.

Refinement

All H atoms were placed in idealized positions and constrained to ride on their parent atoms (C—H 0.93–0.97 Å), with U_{iso}(H) values set at 1.5 U_{eq}(C)(for CH3) or 1.2 U_{eq}(C)(for CH2, thiazole CH).

Figures

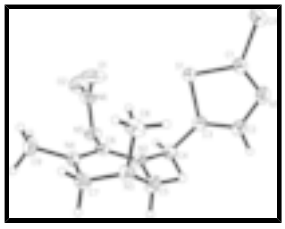

Fig. 1. View of the title compound (I), with displacement ellipsoids drawn at the 30% probability level.

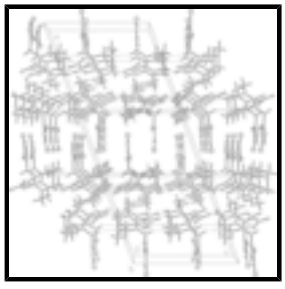

Fig. 2. A packing diagram viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

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Crystal data

$C_9H_{13}ClN_6O_2S$	F_{000} = 1264
M_r = 304.76	D_x = 1.513 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 2652 reflections
a = 32.864 (7) Å	θ = 2.6–25.6º
b = 6.4063 (13) Å	μ = 0.45 mm^{-1}
c = 13.569 (3) Å	*T* = 293 (2) K
β = 110.53 (3)º	Block, colourless
V = 2675.3 (11) Å^3	0.32 × 0.22 × 0.10 mm
Z = 8	

Data collection

Rigaku R-AXIS RAPID IP area-detector diffractometer	2363 independent reflections
Radiation source: Rotating Anode	1985 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.033
T = 153(2) K	θ_{max} = 25.0º
ω Oscillation scans	θ_{min} = 3.0º
Absorption correction: multi-scan (ABSCOR; Higashi 1995)	*h* = −38→38
T_{min} = 0.869, T_{max} = 0.956	*k* = −7→7
9419 measured reflections	*l* = −16→14

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0788P)^2 + 1.7911P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.145$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.17$	$\Delta\rho_{max} = 0.38$ e Å^{-3}
2363 reflections	$\Delta\rho_{min} = -0.33$ e Å^{-3}
173 parameters	Extinction correction: SHELXL, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0107 (11)
Secondary atom site location: difference Fourier map	

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 $F^2 > 2$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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.06171 (2)	0.27878 (12)	0.16669 (7)	0.0561 (3)
Cl1	−0.03042 (2)	0.41507 (14)	0.09448 (8)	0.0715 (3)
C1	0.00747 (8)	0.2188 (4)	0.1269 (2)	0.0456 (6)
N1	−0.00266 (8)	0.0260 (4)	0.1214 (2)	0.0551 (6)
O1	0.15917 (9)	0.4743 (4)	0.2334 (2)	0.0874 (9)
N2	0.14362 (6)	−0.0081 (3)	0.15051 (14)	0.0355 (5)
C2	0.03521 (9)	−0.0889 (5)	0.1509 (2)	0.0541 (7)
H2A	0.0346	−0.2340	0.1520	0.065*
O2	0.19505 (9)	0.4278 (4)	0.40121 (19)	0.0825 (8)
N3	0.14082 (7)	0.0518 (3)	−0.02674 (15)	0.0415 (5)
C3	0.07300 (8)	0.0158 (4)	0.17781 (18)	0.0378 (6)
N4	0.20026 (6)	0.1676 (3)	0.12543 (16)	0.0403 (5)
C4	0.11820 (8)	−0.0718 (4)	0.21546 (19)	0.0408 (6)
H4A	0.1332	−0.0265	0.2873	0.049*
H4B	0.1165	−0.2230	0.2157	0.049*
N5	0.19224 (7)	0.1754 (3)	0.29169 (16)	0.0456 (6)

C5	0.13045 (9)	−0.0922 (4)	0.04226 (19)	0.0470 (7)
H5B	0.1452	−0.2236	0.0432	0.056*
H5C	0.0994	−0.1189	0.0160	0.056*
C6	0.17769 (7)	0.1185 (4)	0.18622 (17)	0.0333 (5)
N6	0.18187 (8)	0.3633 (4)	0.30871 (19)	0.0527 (6)
C7	0.18655 (8)	0.0946 (4)	0.01513 (19)	0.0454 (6)
H7A	0.1935	0.2005	−0.0275	0.054*
H7B	0.2025	−0.0311	0.0118	0.054*
C8	0.11418 (10)	0.2411 (5)	−0.0471 (2)	0.0559 (8)
H8A	0.1225	0.3313	−0.0932	0.084*
H8B	0.1184	0.3120	0.0181	0.084*
H8C	0.0841	0.2041	−0.0795	0.084*
C9	0.23765 (9)	0.3080 (5)	0.1597 (3)	0.0594 (8)
H9A	0.2435	0.3482	0.2315	0.089*
H9B	0.2315	0.4301	0.1159	0.089*
H9C	0.2626	0.2380	0.1541	0.089*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0366 (4)	0.0366 (4)	0.0967 (6)	−0.0027 (3)	0.0252 (4)	−0.0049 (3)
Cl1	0.0430 (4)	0.0628 (6)	0.1085 (7)	0.0110 (3)	0.0262 (4)	0.0014 (4)
C1	0.0374 (13)	0.0489 (16)	0.0538 (15)	−0.0002 (12)	0.0200 (12)	−0.0001 (12)
N1	0.0405 (12)	0.0520 (15)	0.0704 (15)	−0.0082 (11)	0.0165 (11)	0.0040 (12)
O1	0.105 (2)	0.0537 (14)	0.0933 (18)	0.0394 (15)	0.0215 (16)	−0.0055 (13)
N2	0.0382 (11)	0.0361 (11)	0.0352 (10)	−0.0033 (9)	0.0167 (8)	−0.0010 (8)
C2	0.0520 (17)	0.0361 (15)	0.0735 (18)	−0.0093 (12)	0.0211 (14)	0.0036 (13)
O2	0.1016 (19)	0.0792 (18)	0.0685 (14)	−0.0091 (14)	0.0320 (13)	−0.0434 (13)
N3	0.0451 (12)	0.0470 (13)	0.0362 (10)	−0.0016 (10)	0.0188 (9)	−0.0025 (9)
C3	0.0409 (13)	0.0387 (14)	0.0375 (12)	−0.0007 (11)	0.0183 (10)	0.0041 (10)
N4	0.0339 (10)	0.0429 (12)	0.0461 (11)	−0.0048 (9)	0.0165 (9)	−0.0043 (9)
C4	0.0444 (14)	0.0400 (14)	0.0426 (13)	0.0043 (11)	0.0209 (11)	0.0103 (11)
N5	0.0539 (14)	0.0410 (12)	0.0371 (11)	0.0073 (10)	0.0098 (10)	−0.0071 (9)
C5	0.0559 (16)	0.0464 (16)	0.0426 (13)	−0.0155 (13)	0.0223 (12)	−0.0121 (11)
C6	0.0331 (12)	0.0303 (12)	0.0352 (11)	0.0089 (10)	0.0104 (9)	0.0018 (9)
N6	0.0506 (13)	0.0488 (14)	0.0603 (14)	0.0043 (12)	0.0213 (11)	−0.0158 (12)
C7	0.0460 (14)	0.0533 (16)	0.0440 (13)	−0.0004 (12)	0.0247 (11)	−0.0040 (11)
C8	0.0573 (18)	0.067 (2)	0.0438 (14)	0.0142 (15)	0.0177 (13)	0.0042 (13)
C9	0.0440 (15)	0.064 (2)	0.0733 (19)	−0.0178 (14)	0.0239 (14)	−0.0106 (15)

Geometric parameters (Å, °)

S1—C1	1.715 (3)	N4—C9	1.461 (3)
S1—C3	1.720 (3)	N4—C7	1.479 (3)
Cl1—C1	1.715 (3)	C4—H4A	0.9700
C1—N1	1.275 (4)	C4—H4B	0.9700
N1—C2	1.379 (4)	N5—N6	1.294 (3)
O1—N6	1.254 (3)	N5—C6	1.389 (3)
N2—C6	1.329 (3)	C5—H5B	0.9700

N2—C4	1.469 (3)	C5—H5C	0.9700
N2—C5	1.480 (3)	C7—H7A	0.9700
C2—C3	1.344 (4)	C7—H7B	0.9700
C2—H2A	0.9300	C8—H8A	0.9600
O2—N6	1.246 (3)	C8—H8B	0.9600
N3—C7	1.434 (3)	C8—H8C	0.9600
N3—C5	1.438 (3)	C9—H9A	0.9600
N3—C8	1.464 (3)	C9—H9B	0.9600
C3—C4	1.500 (3)	C9—H9C	0.9600
N4—C6	1.326 (3)		
C1—S1—C3	88.66 (13)	N2—C5—H5B	109.4
N1—C1—Cl1	123.0 (2)	N3—C5—H5C	109.4
N1—C1—S1	117.2 (2)	N2—C5—H5C	109.4
Cl1—C1—S1	119.85 (17)	H5B—C5—H5C	108.0
C1—N1—C2	108.0 (2)	N4—C6—N2	120.1 (2)
C6—N2—C4	122.32 (19)	N4—C6—N5	120.9 (2)
C6—N2—C5	120.00 (19)	N2—C6—N5	118.5 (2)
C4—N2—C5	117.67 (19)	O2—N6—O1	122.0 (3)
C3—C2—N1	117.8 (3)	O2—N6—N5	117.9 (3)
C3—C2—H2A	121.1	O1—N6—N5	120.1 (2)
N1—C2—H2A	121.1	N3—C7—N4	111.47 (19)
C7—N3—C5	108.6 (2)	N3—C7—H7A	109.3
C7—N3—C8	113.0 (2)	N4—C7—H7A	109.3
C5—N3—C8	113.1 (2)	N3—C7—H7B	109.3
C2—C3—C4	128.0 (3)	N4—C7—H7B	109.3
C2—C3—S1	108.3 (2)	H7A—C7—H7B	108.0
C4—C3—S1	123.62 (19)	N3—C8—H8A	109.5
C6—N4—C9	122.7 (2)	N3—C8—H8B	109.5
C6—N4—C7	121.1 (2)	H8A—C8—H8B	109.5
C9—N4—C7	116.1 (2)	N3—C8—H8C	109.5
N2—C4—C3	113.29 (19)	H8A—C8—H8C	109.5
N2—C4—H4A	108.9	H8B—C8—H8C	109.5
C3—C4—H4A	108.9	N4—C9—H9A	109.5
N2—C4—H4B	108.9	N4—C9—H9B	109.5
C3—C4—H4B	108.9	H9A—C9—H9B	109.5
H4A—C4—H4B	107.7	N4—C9—H9C	109.5
N6—N5—C6	114.3 (2)	H9A—C9—H9C	109.5
N3—C5—N2	111.0 (2)	H9B—C9—H9C	109.5
N3—C5—H5B	109.4		
C3—S1—C1—N1	0.1 (2)	C9—N4—C6—N2	179.1 (2)
C3—S1—C1—Cl1	−178.89 (18)	C7—N4—C6—N2	4.0 (3)
Cl1—C1—N1—C2	178.9 (2)	C9—N4—C6—N5	−9.2 (4)
S1—C1—N1—C2	−0.1 (3)	C7—N4—C6—N5	175.6 (2)
C1—N1—C2—C3	0.0 (4)	C4—N2—C6—N4	178.4 (2)
N1—C2—C3—C4	178.0 (2)	C5—N2—C6—N4	−0.8 (3)
N1—C2—C3—S1	0.1 (3)	C4—N2—C6—N5	6.5 (3)
C1—S1—C3—C2	−0.1 (2)	C5—N2—C6—N5	−172.7 (2)
C1—S1—C3—C4	−178.1 (2)	N6—N5—C6—N4	84.1 (3)

C6—N2—C4—C3	112.1 (3)	N6—N5—C6—N2	−104.1 (3)
C5—N2—C4—C3	−68.7 (3)	C6—N5—N6—O2	−177.7 (2)
C2—C3—C4—N2	123.3 (3)	C6—N5—N6—O1	2.4 (4)
S1—C3—C4—N2	−59.1 (3)	C5—N3—C7—N4	−54.3 (3)
C7—N3—C5—N2	57.2 (3)	C8—N3—C7—N4	72.1 (3)
C8—N3—C5—N2	−69.0 (3)	C6—N4—C7—N3	24.6 (3)
C6—N2—C5—N3	−30.6 (3)	C9—N4—C7—N3	−150.9 (2)
C4—N2—C5—N3	150.1 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4A···N3^{i}	0.97	2.45	3.314 (3)	148
C4—H4B···O1^{ii}	0.97	2.36	3.178 (3)	142
C7—H7A···O2^{iii}	0.97	2.58	3.483 (4)	156

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

Fig. 1

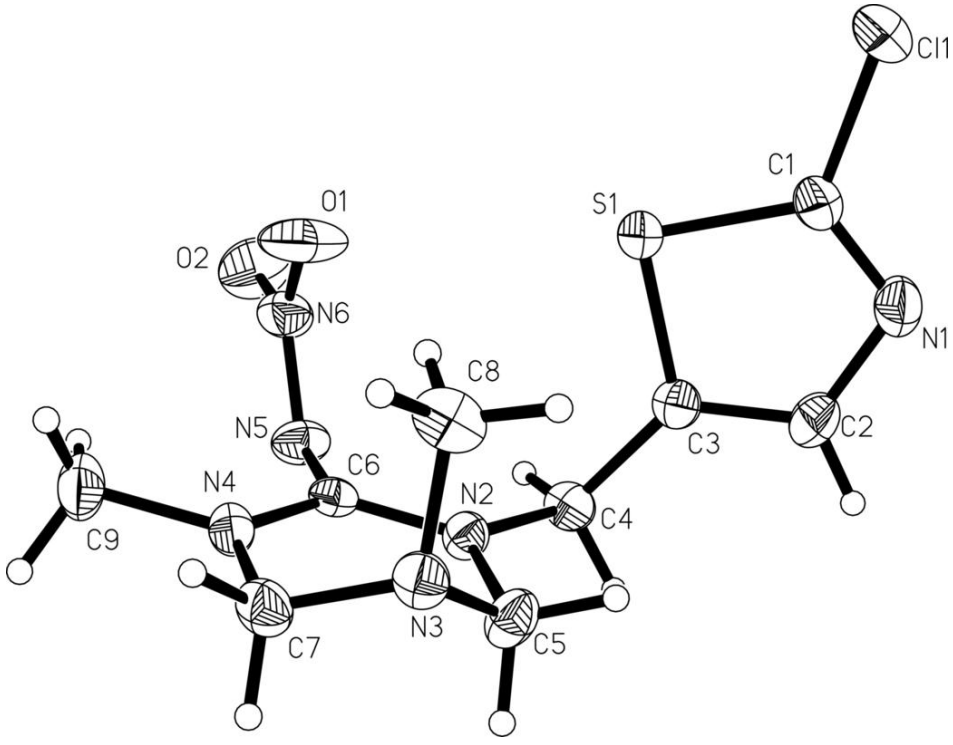

Fig. 2