Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethyl 1-[(2-chloro-1,3-thiazol-5-yl)-methyl]-5-methyl-1*H*-1,2,3-triazole-4-carboxylate

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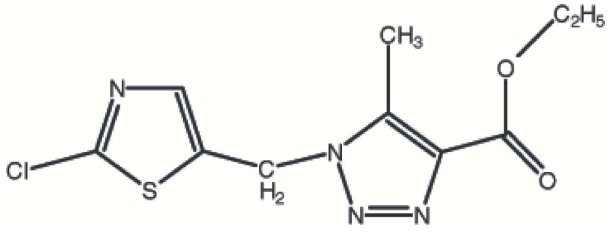
Received 12 November 2008; accepted 14 November 2008

Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.004 Å; R factor = 0.041; wR factor = 0.118; data-to-parameter ratio = 14.1.

In the title compound, $C_{10}H_{11}ClN_4O_2S$, the triazole ring carries methyl and ethoxycarbonyl groups and is bound *via* a methylene bridge to a chlorothiazole unit. There is also evidence for significant electron delocalization in the triazolyl system. Intra- and intermolecular C—H···O hydrogen bonds together with strong π–π stacking interactions [centroid–centroid distance 3.620 (1) Å] stabilize the structure.

Related literature

Many derivatives of triazole have been prepared, and their biological activities have been studied by Ogura *et al.* (2000), Najim *et al.* (2004), Abu-Orabi *et al.* (1989), Shuto *et al.* (1995), Fan & Katritsky (1996), Chen *et al.* (2005) and Liu *et al.* (2001). For the synthesis, see: Chen *et al.* (2007); Chen & Shi (2008). For bond-length data, see: Sasada (1984); Wang *et al.* (1998). For related literature, see: Chen *et al.* (2007); Tian *et al.* (2008); Chen *et al.* (2008); Knox & Rogers (1989); Rogers *et al.* (1985); Shuto *et al.* (1995).



Experimental

Crystal data

$C_{10}H_{11}ClN_4O_2S$
M_r = 286.74
Triclinic, $P\overline{1}$
a = 7.9692 (14) Å
b = 9.1656 (16) Å
c = 10.4430 (18) Å
α = 65.892 (2)°
β = 67.938 (2)°
γ = 80.641 (2)°
V = 645.23 (19) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.46 mm^{-1}
T = 291 (2) K
0.50 × 0.40 × 0.30 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: none
4630 measured reflections
2332 independent reflections
2005 reflections with $I > 2\sigma(I)$
R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.118
S = 1.04
2332 reflections
165 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O1^{i}	0.93	2.47	3.375 (4)	164
C7—H7B···O2	0.96	2.43	3.033 (4)	121

Symmetry code: (i) $x-1, y, z$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); 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*.

The authors gratefully acknowledge financial support of this work by Yunyang Medical College, and acknowledge the Sophisticated Analytical Instrument Facility, Central China Normal University, Whuhan, for the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2677).

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supporting information

Acta Cryst. (2008). E**64**, o2402–o2403 [doi:10.1107/S1600536808037914]

Ethyl 1-[(2-chloro-1,3-thiazol-5-yl)methyl]-5-methyl-1*H*-1,2,3-triazole-4-carboxylate

Xiao-Bao Chen, Feng-Mei Sun, Jing Xu, Zuan Ma and Ai-Hua Zheng

S1. Comment

It is well known that many triazole-related molecules play an important role in the development of agrochemicals such as insecticides, nematocides, acaricide and plant growth regulators (Ogura *et al.*, 2000; Najim *et al.*, 2004; Abu-Orabi *et al.*, 1989; Shuto *et al.*,1995; Fan & Katritsky, 1996; Chen *et al.*, 2005; Richard & Ben, 1985; Ingrid *et al.,* 1989 and Liu *et al.*, 2001). Since the structure-activity relationship is very useful in the rational design of pharmaceuticals and agrochemicals. We report here the crystal structure of the title compound, (I) (Fig. 1), which was synthesized by introducing pyridine rings into a 1,2,3-triazole molecular framework.

In the title compound, the C5—N2 and C6—N4 bonds are significantly shorter than that of the single bond of C—N (1.47 Å; Sasada, 1984) and close to the value of the double bond of C—N (1.28 Å; Wang *et al.*, 1998). This indicates significant electron delocalization in the triazolyl system.

Inter and intramolecular C—H···O hydrogen bonds contribute strongly to the stability of the molecular configuration (Fig.2). Strong π—π stacking interactions are also found between adjacent S1—C1/N1/C2—C3 rings with centroid-centroid distances 3.620 (1) Å, dihedral angles of 0.03 (1)°, and a shortest interplanar distance of 3.573 Å.

S2. Experimental

Ethyl acetylacetate (2 mmol) and 5-azidomethyl-2-chlorothiazole (2 mmol) were added to a suspension of milled potassium carbonate (2 mmol) in DMSO (10 ml). The mixture was stirred at room temperature for 6 h (monitored by thin-layer chromatography) and poured to water (50 ml). The solid was collected by filtration, washed with water and di-ethyl ether, respectively, and dried to give 0.52 g of the title compound (yield 91%). Colourless crystals of (I) suitable for X-ray structure analysis were grown from acetone and petroleum ether (1:1, *v*/*v*).

S3. Refinement

H atoms bonded to C were placed at calculated positions, with C—H distances in the range 0.93 - 0.98Å. They were refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(C), or 1.5U_{eq}(methyl C).

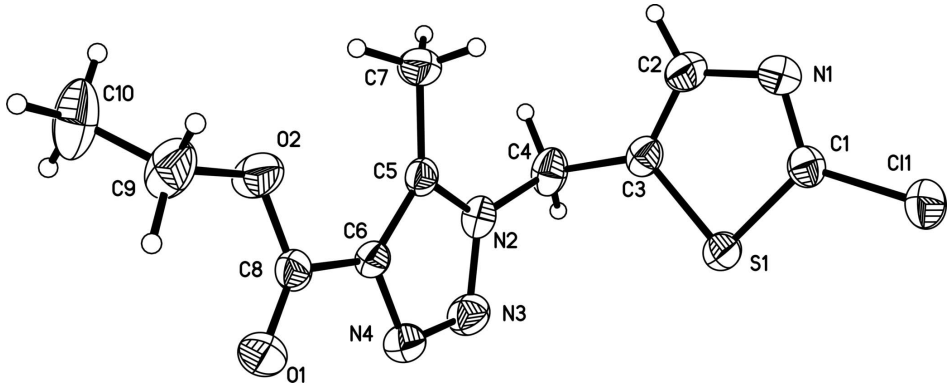

Figure 1

View of the molecular structure of (I), showing the atom labelling scheme and with displacement ellipsoids drawn at the 50% probability level.

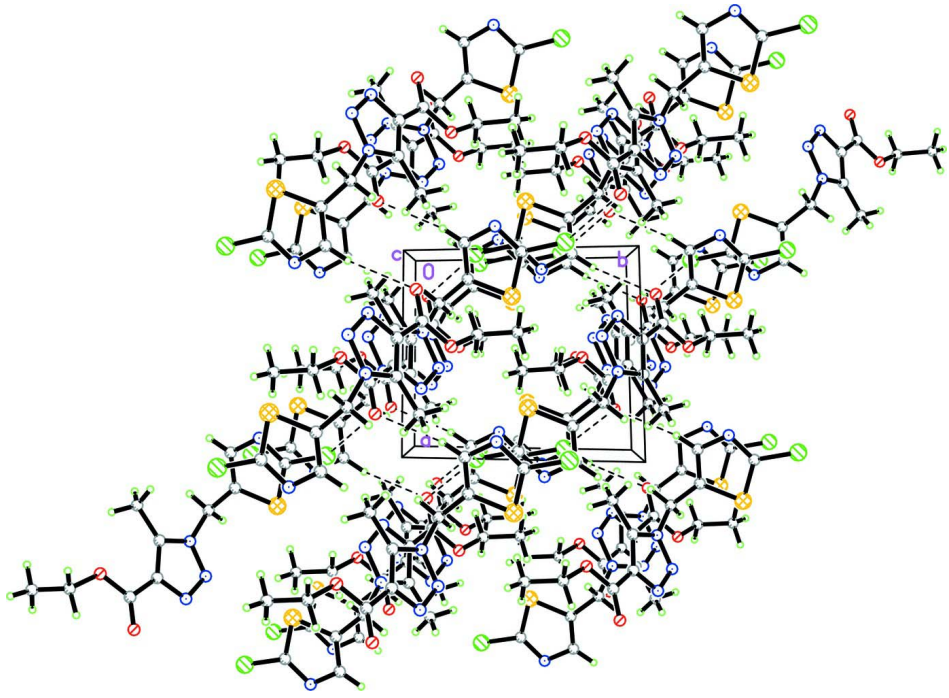

Figure 2

A partial view of the crystal packing of (I), showing the formation of C—H···O hydrogen-bonding interactions (dashed lines).

Ethyl 1-[(2-chloro-1,3-thiazol-5-yl)methyl]-5-methyl-1*H*-1,2,3- triazole-4-carboxylate

Crystal data

$C_{10}H_{11}ClN_4O_2S$
$M_r = 286.74$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.9692\ (14)$ Å
$b = 9.1656\ (16)$ Å
$c = 10.4430\ (18)$ Å
$\alpha = 65.892\ (2)°$
$\beta = 67.938\ (2)°$
$\gamma = 80.641\ (2)°$
$V = 645.23\ (19)$ Å^3
$Z = 2$
$F(000) = 296$
$D_x = 1.476$ Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2592 reflections
θ = 2.4–27.4°
μ = 0.46 mm^{-1}
T = 291 K
Block, colourless
0.50 × 0.40 × 0.30 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
4630 measured reflections
2332 independent reflections
2005 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 25.5°, θ_{min} = 2.4°
h = −9→9
k = −11→11
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.118
S = 1.04
2332 reflections
165 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
$w = 1/[\sigma^2(F_o^2) + (0.062P)^2 + 0.2829P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 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}
Cl1	−0.01266 (10)	0.69136 (8)	0.20124 (9)	0.0704 (2)
S1	0.23526 (8)	0.46808 (7)	0.07021 (7)	0.0534 (2)
O1	0.7825 (3)	−0.0891 (2)	0.3892 (2)	0.0715 (5)
O2	0.5259 (3)	−0.2272 (2)	0.5002 (2)	0.0718 (6)
N1	−0.0923 (3)	0.4021 (3)	0.2475 (3)	0.0674 (6)
N2	0.4074 (3)	0.0929 (2)	0.1275 (2)	0.0486 (5)
N3	0.5752 (3)	0.1573 (3)	0.0531 (2)	0.0603 (5)
N4	0.6709 (3)	0.0880 (2)	0.1400 (2)	0.0567 (5)
C1	0.0281 (3)	0.5109 (3)	0.1813 (3)	0.0496 (5)

C2	−0.0196 (4)	0.2725 (3)	0.2086 (3)	0.0676 (7)
H2	−0.0873	0.1816	0.2446	0.081*
C3	0.1528 (3)	0.2836 (3)	0.1165 (3)	0.0479 (5)
C4	0.2660 (4)	0.1603 (3)	0.0601 (3)	0.0584 (6)
H4A	0.1887	0.0750	0.0830	0.070*
H4B	0.3222	0.2087	−0.0476	0.070*
C5	0.3935 (3)	−0.0189 (2)	0.2639 (2)	0.0419 (5)
C6	0.5634 (3)	−0.0210 (2)	0.2704 (2)	0.0435 (5)
C7	0.2239 (3)	−0.1066 (3)	0.3707 (3)	0.0611 (7)
H7A	0.1451	−0.0411	0.4214	0.092*
H7B	0.2521	−0.2038	0.4424	0.092*
H7C	0.1648	−0.1314	0.3172	0.092*
C8	0.6388 (3)	−0.1135 (3)	0.3903 (3)	0.0472 (5)
C9	0.5797 (5)	−0.3295 (3)	0.6289 (4)	0.0808 (9)
H9A	0.6961	−0.2958	0.6163	0.097*
H9B	0.4914	−0.3195	0.7191	0.097*
C10	0.5916 (6)	−0.4920 (4)	0.6429 (4)	0.1001 (13)
H10A	0.4813	−0.5209	0.6427	0.150*
H10B	0.6104	−0.5599	0.7349	0.150*
H10C	0.6913	−0.5045	0.5605	0.150*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0673 (4)	0.0627 (4)	0.0875 (5)	0.0081 (3)	−0.0224 (4)	−0.0417 (4)
S1	0.0525 (4)	0.0453 (3)	0.0548 (4)	−0.0034 (3)	−0.0102 (3)	−0.0180 (3)
O1	0.0572 (11)	0.0679 (12)	0.0968 (14)	−0.0051 (9)	−0.0423 (10)	−0.0223 (10)
O2	0.0735 (12)	0.0639 (11)	0.0695 (11)	−0.0188 (9)	−0.0428 (10)	0.0060 (9)
N1	0.0479 (12)	0.0600 (13)	0.0824 (15)	−0.0036 (10)	−0.0144 (11)	−0.0218 (12)
N2	0.0597 (12)	0.0394 (9)	0.0494 (10)	0.0052 (9)	−0.0230 (9)	−0.0176 (8)
N3	0.0638 (13)	0.0530 (12)	0.0515 (11)	−0.0068 (10)	−0.0123 (10)	−0.0125 (9)
N4	0.0518 (11)	0.0514 (11)	0.0573 (12)	−0.0067 (9)	−0.0114 (9)	−0.0157 (10)
C1	0.0496 (12)	0.0485 (12)	0.0504 (12)	0.0045 (10)	−0.0207 (10)	−0.0174 (10)
C2	0.0589 (16)	0.0488 (14)	0.092 (2)	−0.0081 (12)	−0.0286 (14)	−0.0188 (14)
C3	0.0576 (14)	0.0418 (11)	0.0486 (12)	0.0006 (10)	−0.0291 (11)	−0.0117 (10)
C4	0.0796 (17)	0.0483 (13)	0.0613 (15)	0.0104 (12)	−0.0412 (13)	−0.0229 (12)
C5	0.0455 (11)	0.0347 (10)	0.0480 (11)	0.0035 (9)	−0.0177 (9)	−0.0182 (9)
C6	0.0433 (11)	0.0354 (10)	0.0499 (12)	−0.0012 (9)	−0.0128 (9)	−0.0171 (9)
C7	0.0465 (13)	0.0571 (15)	0.0709 (16)	−0.0079 (11)	−0.0228 (12)	−0.0108 (12)
C8	0.0464 (12)	0.0397 (11)	0.0621 (14)	0.0046 (10)	−0.0221 (10)	−0.0243 (10)
C9	0.109 (2)	0.0618 (17)	0.0772 (19)	−0.0068 (17)	−0.0621 (19)	−0.0026 (15)
C10	0.162 (4)	0.068 (2)	0.098 (2)	0.034 (2)	−0.087 (3)	−0.0328 (18)

Geometric parameters (Å, º)

Cl1—C1	1.715 (2)	C3—C4	1.501 (3)
S1—C1	1.717 (2)	C4—H4A	0.9700
S1—C3	1.726 (2)	C4—H4B	0.9700

O1—C8	1.197 (3)	C5—C6	1.378 (3)
O2—C8	1.328 (3)	C5—C7	1.485 (3)
O2—C9	1.464 (3)	C6—C8	1.476 (3)
N1—C1	1.281 (3)	C7—H7A	0.9600
N1—C2	1.380 (4)	C7—H7B	0.9600
N2—C5	1.349 (3)	C7—H7C	0.9600
N2—N3	1.357 (3)	C9—C10	1.427 (5)
N2—C4	1.470 (3)	C9—H9A	0.9700
N3—N4	1.304 (3)	C9—H9B	0.9700
N4—C6	1.370 (3)	C10—H10A	0.9600
C2—C3	1.340 (4)	C10—H10B	0.9600
C2—H2	0.9300	C10—H10C	0.9600

C1—S1—C3	88.37 (12)	C6—C5—C7	133.6 (2)
C8—O2—C9	118.2 (2)	N4—C6—C5	109.60 (19)
C1—N1—C2	108.7 (2)	N4—C6—C8	119.0 (2)
C5—N2—N3	111.70 (19)	C5—C6—C8	131.4 (2)
C5—N2—C4	129.3 (2)	C5—C7—H7A	109.5
N3—N2—C4	118.8 (2)	C5—C7—H7B	109.5
N4—N3—N2	107.38 (18)	H7A—C7—H7B	109.5
N3—N4—C6	108.2 (2)	C5—C7—H7C	109.5
N1—C1—Cl1	122.4 (2)	H7A—C7—H7C	109.5
N1—C1—S1	116.79 (19)	H7B—C7—H7C	109.5
Cl1—C1—S1	120.83 (14)	O1—C8—O2	124.3 (2)
C3—C2—N1	117.0 (2)	O1—C8—C6	124.5 (2)
C3—C2—H2	121.5	O2—C8—C6	111.18 (18)
N1—C2—H2	121.5	C10—C9—O2	110.0 (3)
C2—C3—C4	128.2 (2)	C10—C9—H9A	109.7
C2—C3—S1	109.13 (19)	O2—C9—H9A	109.7
C4—C3—S1	122.70 (19)	C10—C9—H9B	109.7
N2—C4—C3	111.66 (18)	O2—C9—H9B	109.7
N2—C4—H4A	109.3	H9A—C9—H9B	108.2
C3—C4—H4A	109.3	C9—C10—H10A	109.5
N2—C4—H4B	109.3	C9—C10—H10B	109.5
C3—C4—H4B	109.3	H10A—C10—H10B	109.5
H4A—C4—H4B	107.9	C9—C10—H10C	109.5
N2—C5—C6	103.16 (19)	H10A—C10—H10C	109.5
N2—C5—C7	123.2 (2)	H10B—C10—H10C	109.5

C5—N2—N3—N4	0.1 (3)	C4—N2—C5—C6	−173.8 (2)
C4—N2—N3—N4	174.52 (19)	N3—N2—C5—C7	178.8 (2)
N2—N3—N4—C6	−0.1 (3)	C4—N2—C5—C7	5.1 (3)
C2—N1—C1—Cl1	179.52 (19)	N3—N4—C6—C5	0.0 (3)
C2—N1—C1—S1	−0.5 (3)	N3—N4—C6—C8	−178.4 (2)
C3—S1—C1—N1	0.1 (2)	N2—C5—C6—N4	0.0 (2)
C3—S1—C1—Cl1	−179.93 (15)	C7—C5—C6—N4	−178.6 (2)
C1—N1—C2—C3	0.8 (4)	N2—C5—C6—C8	178.2 (2)
N1—C2—C3—C4	178.2 (2)	C7—C5—C6—C8	−0.4 (4)

N1—C2—C3—S1	−0.8 (3)	C9—O2—C8—O1	0.2 (4)
C1—S1—C3—C2	0.38 (19)	C9—O2—C8—C6	−179.5 (2)
C1—S1—C3—C4	−178.66 (19)	N4—C6—C8—O1	8.3 (3)
C5—N2—C4—C3	78.7 (3)	C5—C6—C8—O1	−169.7 (2)
N3—N2—C4—C3	−94.6 (3)	N4—C6—C8—O2	−171.9 (2)
C2—C3—C4—N2	−109.0 (3)	C5—C6—C8—O2	10.0 (3)
S1—C3—C4—N2	69.9 (3)	C8—O2—C9—C10	−119.0 (3)
N3—N2—C5—C6	−0.1 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O1^{i}	0.93	2.47	3.375 (4)	164
C7—H7*B*···O2	0.96	2.43	3.033 (4)	121
C9—H9*A*···O1	0.97	2.28	2.710 (4)	106

Symmetry code: (i) *x*−1, *y*, *z*.