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2-{3-[1-(3,4-Dichlorophenyl)ethyl]-1,3-thiazolidin-2-ylidene}malononitrile

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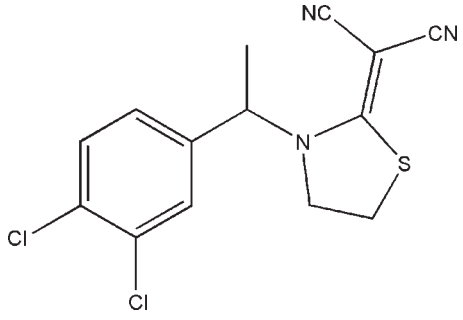
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.004 Å; R factor = 0.047; wR factor = 0.102; data-to-parameter ratio = 13.7.

In the title compound, $C_{14}H_{11}Cl_2N_3S$, the thiazole ring is in an envelope conformation with the $-CH_2-$ group bonded to the S atom forming the flap. The crystal structure is stabilized by weak intermolecular C—H···Cl and C—H···N hydrogen bonds.

Related literature

For the biological activity of thiazole componds, see: Hense *et al.* (2002). For the synthesis of the title compound, see: Jeschke *et al.* (2002). For a related structure, see: Cunico, *et al.* (2007).



Experimental

Crystal data

$C_{14}H_{11}Cl_2N_3S$
M_r = 324.22
Monoclinic, $P2_1/n$
a = 7.5900 (15) Å
b = 14.957 (3) Å
c = 12.783 (3) Å
β = 99.03 (3)°
V = 1433.2 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.59 mm^{-1}
T = 113 K
0.14 × 0.12 × 0.10 mm

Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.922, T_{max} = 0.943
8837 measured reflections
2493 independent reflections
2374 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.102
S = 1.17
2493 reflections
182 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.98 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3A···N3^{i}	0.99	2.57	3.477 (4)	153
C7—H7A···Cl2^{ii}	1.00	2.83	3.623 (3)	137

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, -y+1, -z$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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: LH5066).

References

Cunico, W., Gomes, C. R. B., Wardell, S. M. S. V., Low, J. N. & Glidewell, C. (2007). *Acta Cryst.* C**63**, o411–o414.
Hense, A., Fischer, R. & Gesing, E. R. (2002). WO Patent 2002096872.
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Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
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supplementary materials

Acta Cryst. (2010). E**66**, o1827 [**doi:10.1107/S1600536810024049**]

2-{3-[1-(3,4-Dichlorophenyl)ethyl]-1,3-thiazolidin-2-ylidene}malononitrile

X. Zhang, H. Li and L. Xu

Comment

Recently, compounds containing the 2-(thiazolidin-2-ylidene)malononitrile group have attracted much interest because compounds containing a thiazole ring system are well known as efficient insecticides and pesticides (Hense, *et al.*, 2002). In an attempt to synthesize these types of compounds with higher biological activity the title compound (I) was synthesized and its crystal structure is reported herein.

In (I) (Fig. 1), the bond lengths angles are normal and in a agreement with those common to a previously reported structure (Cunico, *et al.*, 2007). The thiazole ring is in an envelope conformation with the -CH_2- group bonded to the S atom forming the flap. The crystal structure is stabilized by weak intermolecular C—H···Cl and C—H···N hydrogen bonds.

Experimental

Following the procedure of Jeschke, *et al.* (2002) 2-(thiazolidin-2-ylidene)malononitrile 15.1 g(0.10 mol) and potassium carbonate 16.6 g(0.12 mmol) were dissolved in *N*,*N*-dimethylformamide(DMF) (55 ml) and stirred 0.5 h at room temperature. Then 1,2-dichloro-4-(1-chloroethyl)benzene 20.9 g (0.10 mmol) was added, dropwise within 2 h at 318 K. The mixture was then stirred for 8 h at 358 K. After cooling at room temperature, 20 ml of water was added. The mixture was extracted with CH_2Cl_2 (15 ml) and the organic layer was washed with water and dried over anhydrous sodium sulfate. The excess CH_2Cl_2 was removed on a water vacuum pump obtaining the oily product which was rerystallized from methanol to afford the title compound 26.8 g (83% yield). Single crystals suitable for X-ray measurement were obtained by recrystallization of the title compound from a mixture of acetone and methanol at room temperature.

Refinement

All C-bound H atoms were placed in calculated positions, with C—H = 0.95–1.00 Å, and included in the final cycles of refinement using a riding model, with U_{iso}(H) = 1.2U_{eq}(C).

Figures

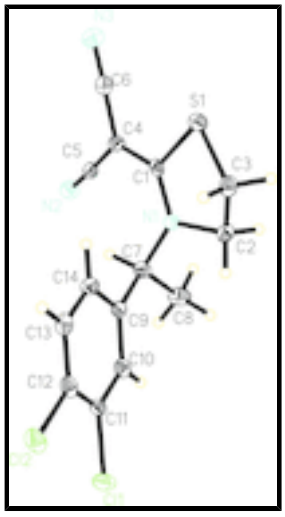

Fig. 1. The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level.

2-{3-[1-(3,4-Dichlorophenyl)ethyl]-1,3-thiazolidin-2-ylidene}malononitrile

Crystal data

$C_{14}H_{11}Cl_2N_3S$	$F(000) = 664$
$M_r = 324.22$	$D_x = 1.503$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 3119 reflections
$a = 7.5900$ (15) Å	$\theta = 2.1$–$27.2°$
$b = 14.957$ (3) Å	$\mu = 0.59$ mm^{-1}
$c = 12.783$ (3) Å	$T = 113$ K
$\beta = 99.03$ (3)°	Prism, black
$V = 1433.2$ (5) Å^3	0.14 × 0.12 × 0.10 mm
$Z = 4$	

Data collection

Rigaku Saturn diffractometer	2493 independent reflections
Radiation source: fine-focus sealed tube	2374 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.032$
Detector resolution: 7.31 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 2.7°$
ω scans	$h = -9 \rightarrow 8$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	$k = -17 \rightarrow 17$
$T_{min} = 0.922$, $T_{max} = 0.943$	$l = -15 \rightarrow 13$
8837 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.047$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.102$	H-atom parameters constrained
$S = 1.17$	$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 2.7247P]$ where $P = (F_o^2 + 2F_c^2)/3$
2493 reflections	$(\Delta/\sigma)_{max} < 0.001$
182 parameters	$\Delta\rho_{max} = 0.98$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.31$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.64889 (9)	0.08386 (5)	−0.14263 (5)	0.01840 (19)
Cl1	0.92712 (10)	0.58799 (5)	0.13883 (6)	0.0241 (2)
Cl2	0.74727 (10)	0.62951 (5)	−0.09604 (6)	0.0243 (2)
N1	0.7016 (3)	0.19511 (15)	0.01236 (18)	0.0156 (5)
N2	0.2888 (3)	0.16439 (17)	0.1598 (2)	0.0228 (6)
N3	0.1985 (3)	0.01685 (18)	−0.1358 (2)	0.0276 (6)
C1	0.5784 (4)	0.13843 (17)	−0.0353 (2)	0.0146 (6)
C2	0.8768 (4)	0.1872 (2)	−0.0228 (2)	0.0194 (6)
H2A	0.9508	0.1414	0.0192	0.023*
H2B	0.9410	0.2450	−0.0150	0.023*
C3	0.8370 (4)	0.1601 (2)	−0.1382 (2)	0.0199 (6)
H3A	0.9408	0.1297	−0.1607	0.024*
H3B	0.8047	0.2127	−0.1843	0.024*
C4	0.4095 (4)	0.11831 (18)	−0.0098 (2)	0.0161 (6)
C5	0.3460 (4)	0.14437 (18)	0.0850 (2)	0.0174 (6)
C6	0.2938 (4)	0.06174 (19)	−0.0798 (2)	0.0184 (6)
C7	0.6790 (4)	0.26246 (19)	0.0927 (2)	0.0177 (6)
H7A	0.5539	0.2575	0.1076	0.021*

C8	0.8041 (4)	0.2423 (2)	0.1955 (2)	0.0242 (7)
H8A	0.7885	0.1800	0.2160	0.036*
H8B	0.7762	0.2821	0.2516	0.036*
H8C	0.9279	0.2518	0.1850	0.036*
C9	0.6999 (4)	0.35513 (18)	0.0458 (2)	0.0158 (6)
C10	0.7943 (4)	0.42212 (19)	0.1048 (2)	0.0178 (6)
H10A	0.8506	0.4103	0.1752	0.021*
C11	0.8072 (4)	0.50688 (18)	0.0613 (2)	0.0173 (6)
C12	0.7274 (4)	0.52438 (19)	−0.0414 (2)	0.0187 (6)
C13	0.6305 (4)	0.45847 (19)	−0.1013 (2)	0.0197 (6)
H13A	0.5743	0.4708	−0.1716	0.024*
C14	0.6165 (4)	0.37428 (19)	−0.0575 (2)	0.0186 (6)
H14A	0.5494	0.3291	−0.0981	0.022*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0204 (4)	0.0169 (4)	0.0180 (4)	0.0004 (3)	0.0032 (3)	−0.0022 (3)
Cl1	0.0280 (4)	0.0179 (4)	0.0271 (4)	−0.0050 (3)	0.0062 (3)	−0.0057 (3)
Cl2	0.0257 (4)	0.0176 (4)	0.0315 (4)	0.0026 (3)	0.0111 (3)	0.0080 (3)
N1	0.0142 (12)	0.0136 (12)	0.0192 (12)	−0.0005 (9)	0.0035 (9)	0.0004 (9)
N2	0.0222 (13)	0.0214 (13)	0.0257 (14)	−0.0027 (10)	0.0068 (11)	0.0004 (11)
N3	0.0236 (14)	0.0267 (15)	0.0314 (15)	−0.0036 (11)	0.0010 (12)	−0.0027 (12)
C1	0.0171 (14)	0.0111 (13)	0.0149 (13)	0.0047 (10)	0.0002 (11)	0.0030 (10)
C2	0.0134 (14)	0.0202 (15)	0.0250 (15)	−0.0009 (11)	0.0038 (11)	−0.0006 (12)
C3	0.0170 (14)	0.0221 (15)	0.0217 (15)	−0.0002 (12)	0.0063 (12)	0.0011 (12)
C4	0.0170 (14)	0.0119 (13)	0.0183 (14)	−0.0010 (11)	−0.0005 (11)	0.0021 (11)
C5	0.0141 (14)	0.0124 (14)	0.0248 (16)	0.0001 (10)	0.0001 (12)	0.0037 (12)
C6	0.0177 (14)	0.0183 (15)	0.0198 (15)	0.0008 (12)	0.0047 (12)	0.0037 (12)
C7	0.0170 (14)	0.0177 (15)	0.0193 (15)	−0.0024 (11)	0.0061 (11)	−0.0039 (11)
C8	0.0330 (17)	0.0201 (15)	0.0191 (15)	−0.0044 (13)	0.0032 (13)	0.0022 (12)
C9	0.0137 (13)	0.0135 (14)	0.0213 (15)	−0.0006 (10)	0.0058 (11)	−0.0005 (11)
C10	0.0168 (14)	0.0203 (15)	0.0174 (14)	0.0020 (11)	0.0059 (11)	−0.0023 (11)
C11	0.0151 (14)	0.0128 (14)	0.0255 (15)	−0.0006 (11)	0.0074 (11)	−0.0044 (11)
C12	0.0186 (14)	0.0162 (14)	0.0232 (15)	0.0030 (11)	0.0095 (12)	0.0035 (12)
C13	0.0178 (14)	0.0222 (15)	0.0195 (15)	0.0039 (12)	0.0040 (11)	0.0016 (12)
C14	0.0149 (14)	0.0186 (15)	0.0219 (15)	−0.0018 (11)	0.0019 (11)	−0.0032 (12)

Geometric parameters (Å, °)

S1—C1	1.751 (3)	C4—C6	1.429 (4)
S1—C3	1.821 (3)	C7—C8	1.526 (4)
Cl1—C11	1.732 (3)	C7—C9	1.528 (4)
Cl2—C12	1.736 (3)	C7—H7A	1.0000
N1—C1	1.336 (3)	C8—H8A	0.9800
N1—C7	1.468 (3)	C8—H8B	0.9800
N1—C2	1.474 (4)	C8—H8C	0.9800
N2—C5	1.150 (4)	C9—C10	1.384 (4)
N3—C6	1.151 (4)	C9—C14	1.402 (4)

C1—C4	1.404 (4)	C10—C11	1.394 (4)
C2—C3	1.514 (4)	C10—H10A	0.9500
C2—H2A	0.9900	C11—C12	1.382 (4)
C2—H2B	0.9900	C12—C13	1.386 (4)
C3—H3A	0.9900	C13—C14	1.389 (4)
C3—H3B	0.9900	C13—H13A	0.9500
C4—C5	1.427 (4)	C14—H14A	0.9500
C1—S1—C3	91.05 (13)	N1—C7—H7A	107.6
C1—N1—C7	127.2 (2)	C8—C7—H7A	107.6
C1—N1—C2	114.2 (2)	C9—C7—H7A	107.6
C7—N1—C2	118.6 (2)	C7—C8—H8A	109.5
N1—C1—C4	129.0 (3)	C7—C8—H8B	109.5
N1—C1—S1	112.0 (2)	H8A—C8—H8B	109.5
C4—C1—S1	119.0 (2)	C7—C8—H8C	109.5
N1—C2—C3	105.5 (2)	H8A—C8—H8C	109.5
N1—C2—H2A	110.6	H8B—C8—H8C	109.5
C3—C2—H2A	110.6	C10—C9—C14	118.9 (3)
N1—C2—H2B	110.6	C10—C9—C7	121.3 (2)
C3—C2—H2B	110.6	C14—C9—C7	119.7 (2)
H2A—C2—H2B	108.8	C9—C10—C11	120.3 (3)
C2—C3—S1	103.50 (19)	C9—C10—H10A	119.9
C2—C3—H3A	111.1	C11—C10—H10A	119.9
S1—C3—H3A	111.1	C12—C11—C10	120.2 (3)
C2—C3—H3B	111.1	C12—C11—Cl1	121.6 (2)
S1—C3—H3B	111.1	C10—C11—Cl1	118.2 (2)
H3A—C3—H3B	109.0	C11—C12—C13	120.3 (3)
C1—C4—C5	125.5 (2)	C11—C12—Cl2	120.0 (2)
C1—C4—C6	118.4 (3)	C13—C12—Cl2	119.6 (2)
C5—C4—C6	115.9 (2)	C12—C13—C14	119.3 (3)
N2—C5—C4	177.5 (3)	C12—C13—H13A	120.3
N3—C6—C4	179.0 (3)	C14—C13—H13A	120.3
N1—C7—C8	110.0 (2)	C13—C14—C9	120.9 (3)
N1—C7—C9	108.5 (2)	C13—C14—H14A	119.6
C8—C7—C9	115.4 (2)	C9—C14—H14A	119.6
C7—N1—C1—C4	−11.5 (4)	C1—N1—C7—C9	−114.5 (3)
C2—N1—C1—C4	169.1 (3)	C2—N1—C7—C9	64.9 (3)
C7—N1—C1—S1	169.1 (2)	N1—C7—C9—C10	−138.4 (3)
C2—N1—C1—S1	−10.3 (3)	C8—C7—C9—C10	−14.5 (4)
C3—S1—C1—N1	−11.7 (2)	N1—C7—C9—C14	44.2 (3)
C3—S1—C1—C4	168.8 (2)	C8—C7—C9—C14	168.0 (3)
C1—N1—C2—C3	32.4 (3)	C14—C9—C10—C11	−0.6 (4)
C7—N1—C2—C3	−147.1 (2)	C7—C9—C10—C11	−178.1 (2)
N1—C2—C3—S1	−37.5 (2)	C9—C10—C11—C12	−0.7 (4)
C1—S1—C3—C2	28.5 (2)	C9—C10—C11—Cl1	−180.0 (2)
N1—C1—C4—C5	−11.2 (5)	C10—C11—C12—C13	1.5 (4)
S1—C1—C4—C5	168.2 (2)	Cl1—C11—C12—C13	−179.3 (2)
N1—C1—C4—C6	173.6 (3)	C10—C11—C12—Cl2	−178.8 (2)
S1—C1—C4—C6	−7.0 (3)	Cl1—C11—C12—Cl2	0.4 (3)

C1—C4—C5—N2	169 (7)	C11—C12—C13—C14	−0.9 (4)
C6—C4—C5—N2	−16 (7)	Cl2—C12—C13—C14	179.4 (2)
C1—C4—C6—N3	−147 (20)	C12—C13—C14—C9	−0.5 (4)
C5—C4—C6—N3	37 (20)	C10—C9—C14—C13	1.2 (4)
C1—N1—C7—C8	118.5 (3)	C7—C9—C14—C13	178.8 (3)
C2—N1—C7—C8	−62.1 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3A···N3^{i}	0.99	2.57	3.477 (4)	153
C7—H7A···Cl2^{ii}	1.00	2.83	3.623 (3)	137

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

Fig. 1