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Ethyl 4-(4-chlorophenyl)-5-cyano-2-methyl-6-sulfanylidene-1,6-dihydropyridine-3-carboxylate

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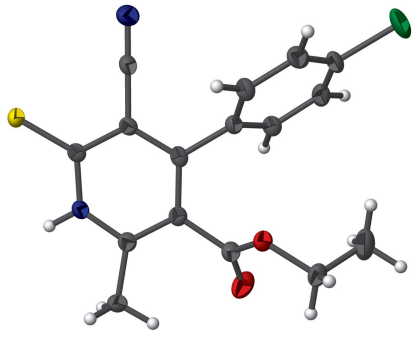
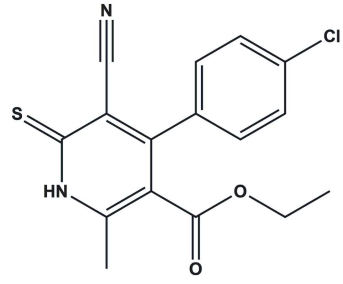
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{16}H_{13}ClN_2O_2S$, the dihedral angle between the 4-chlorophenyl ring and the pyridine ring is 63.53 (6)°. There is an intramolecular C—H···O contact present. In the crystal, molecules are linked by pairs of N—H···S hydrogen bonds, forming inversion dimers. The dimers are linked by C—H···O and C—H···N hydrogen bonds, forming slabs parallel to the *ab* plane.

3D view



Chemical scheme



Structure description

Pyridine scaffold compounds continue to attract great interest due to their wide variety of interesting biological activities. They exhibit anticancer, analgesic, antimicrobial and antidepressant activities (Kumar *et al.*, 2011). In addition, pyridines are used in the pharmaceutical industry as raw materials for various drugs, vitamins and fungicides (Kumar *et al.*, 2011). These facts promoted us to synthesize and determine the crystal structure of the title compound.

In the title compound, Fig. 1, the pyridine and chlorobenzene rings make a dihedral angle of 63.53 (8)° with each other. The C3—C4—C14—O1, C3—C4—C14—O2, C4—C14—O2—C15 and C14—O2—C15—C16 torsion angles are −133.26 (19), 47.2 (2), 179.63 (13) and 88.8 (2)°, respectively. The conformation of the molecule is partially determined by a weak intramolecular C6—H6*A*···O1 contact (Table 1). In the crystal, pairwise N—H···S hydrogen bonds link the molecules to form inversion dimers which further associate *via* C—H···O and C—H···N hydrogen bonds, forming slabs parallel to the *ab* plane (Fig. 2 and Table 1).

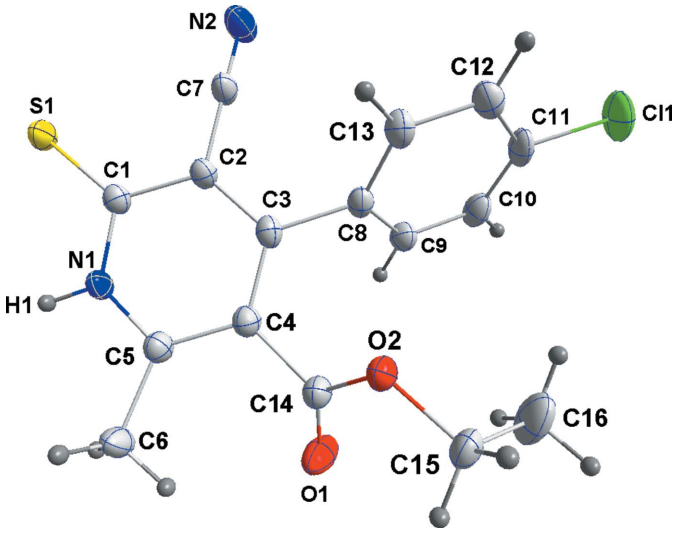


Figure 1
The molecular structure of the title compound, with atom labelling and 50% probability ellipsoids.

Synthesis and crystallization

To a mixture of 4-chlorobenzylidenecyanothioacetamide (2.22 g, 10 mmol) and ethyl acetoacetate (1.3 ml, 10 mmol) in ethanol (35 ml), three drops of piperidine were added. The resulting mixture was heated under reflux for 3 h and then allowed to stand overnight. The solid that separated was collected and recrystallized from ethanol as orange plates of the title compound (yield: 64%; m.p. 528 K). IR (KBr, cm^{-1}) ν = 3200 (NH), 2220 (C≡N), 1700 (C=O). ^{1}H NMR (DMSO-d_6, p.p.m.): δ 13.6 (*s*, 1H, NH), 7.4–7.8 (*dd*, 4H, ArH), 3.8–4.1(*q*, 2H, OCH_2), 2.6 (*s*, 3H, CH_3 at C-6), 0.8–1.0 (*t*, 3H, CH_3)

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

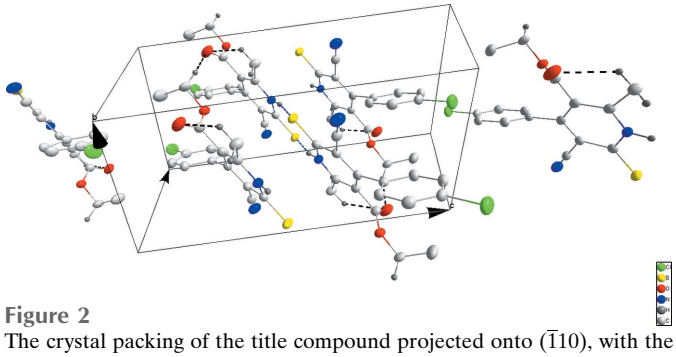


Figure 2
The crystal packing of the title compound projected onto ($\bar{1}$10), with the hydrogen bonds shown as blue and black dashed lines (see Table 1).

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···S1^{i}	0.91	2.40	3.2911 (14)	166
C6—H6A···O1	0.98	2.36	3.047 (2)	127
C6—H6B···N2^{ii}	0.98	2.45	3.305 (2)	145
C15—H15B···O1^{iii}	0.99	2.41	3.327 (2)	153

Symmetry codes: (i) $-x+3, -y+1, -z+1$; (ii) $x+1, y-1, z$; (iii) $x-1, y, z$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{13}ClN_2O_2S$
M_r	332.79
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	150
a, b, c (Å)	5.9498 (2), 8.0999 (2), 16.3919 (4)
α, β, γ (°)	85.990 (1), 81.410 (1), 82.294 (1)
V (Å^3)	773.05 (4)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	3.52
Crystal size (mm)	0.25 × 0.20 × 0.03
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.69, 0.90
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5834, 2833, 2591
R_{int}	0.027
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.105, 1.05
No. of reflections	2833
No. of parameters	201
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.37

Computer programs: *APEX3* (Bruker, 2016), *SAINT* (Bruker, 2016), *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014/7* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012), *SHELXTL* (Sheldrick, 2008).

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160531 [doi:10.1107/S2414314616005319]

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Crystal data

$C_{16}H_{13}ClN_2O_2S$
M_r = 332.79
Triclinic, $P\overline{1}$
a = 5.9498 (2) Å
b = 8.0999 (2) Å
c = 16.3919 (4) Å
α = 85.990 (1)°
β = 81.410 (1)°
γ = 82.294 (1)°
V = 773.05 (4) Å^3
Z = 2
$F(000)$ = 344
D_x = 1.430 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 4687 reflections
θ = 2.7–72.1°
μ = 3.52 mm^{-1}
T = 150 K
Plate, yellow
0.25 × 0.20 × 0.03 mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Radiation source: INCOATEC IμS micro–focus source
Mirror monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)
T_{min} = 0.69, T_{max} = 0.90
5834 measured reflections
2833 independent reflections
2591 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 72.1°, θ_{min} = 2.7°
h = −7→6
k = −9→9
l = −20→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.105
S = 1.05
2833 reflections
201 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0667P)^2 + 0.2083P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.99 Å) while that attached to nitrogen was placed in a location derived from a difference map and its coordinates adjusted to give N—H = 0.91 Å. All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.09171 (9)	0.76572 (7)	0.95570 (3)	0.04561 (17)
S1	1.25779 (7)	0.71159 (5)	0.50649 (2)	0.02518 (14)
O1	0.9605 (2)	0.10792 (18)	0.79003 (9)	0.0391 (3)
O2	0.6182 (2)	0.21882 (14)	0.75633 (7)	0.0241 (3)
N1	1.2163 (2)	0.41120 (16)	0.58006 (8)	0.0217 (3)
H1	1.3513	0.3821	0.5473	0.032*
N2	0.7694 (3)	0.93321 (19)	0.63377 (11)	0.0366 (4)
C1	1.1310 (3)	0.5763 (2)	0.57500 (10)	0.0211 (3)
C2	0.9336 (3)	0.62163 (19)	0.63293 (10)	0.0210 (3)
C3	0.8416 (3)	0.5079 (2)	0.69179 (10)	0.0210 (3)
C4	0.9405 (3)	0.3390 (2)	0.69120 (10)	0.0216 (3)
C5	1.1289 (3)	0.2924 (2)	0.63341 (10)	0.0225 (3)
C6	1.2464 (3)	0.1199 (2)	0.61975 (12)	0.0283 (4)
H6A	1.1775	0.0420	0.6616	0.042*
H6B	1.4095	0.1163	0.6241	0.042*
H6C	1.2294	0.0881	0.5646	0.042*
C7	0.8412 (3)	0.7947 (2)	0.63293 (10)	0.0242 (4)
C8	0.6520 (3)	0.56935 (19)	0.75689 (10)	0.0215 (3)
C9	0.6899 (3)	0.5590 (2)	0.83914 (10)	0.0257 (4)
H9	0.8330	0.5081	0.8535	0.031*
C10	0.5192 (3)	0.6227 (2)	0.90009 (11)	0.0298 (4)
H10	0.5460	0.6186	0.9559	0.036*
C11	0.3092 (3)	0.6923 (2)	0.87861 (11)	0.0287 (4)
C12	0.2688 (3)	0.7062 (2)	0.79737 (11)	0.0290 (4)
H12	0.1248	0.7565	0.7835	0.035*
C13	0.4419 (3)	0.6454 (2)	0.73635 (10)	0.0251 (4)
H13	0.4170	0.6557	0.6802	0.030*
C14	0.8448 (3)	0.2090 (2)	0.75146 (10)	0.0246 (4)
C15	0.5085 (3)	0.0965 (2)	0.81314 (11)	0.0287 (4)
H15A	0.6140	−0.0088	0.8150	0.034*
H15B	0.3684	0.0724	0.7928	0.034*
C16	0.4470 (5)	0.1599 (3)	0.89807 (13)	0.0514 (6)
H16A	0.3688	0.0777	0.9345	0.077*

H16B	0.3453	0.2653	0.8960	0.077*
H16C	0.5866	0.1781	0.9194	0.077*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0386 (3)	0.0553 (3)	0.0385 (3)	−0.0061 (2)	0.0172 (2)	−0.0194 (2)
S1	0.0246 (2)	0.0228 (2)	0.0251 (2)	−0.00264 (15)	0.00473 (17)	0.00094 (15)
O1	0.0257 (7)	0.0429 (8)	0.0452 (8)	−0.0029 (5)	−0.0042 (6)	0.0177 (6)
O2	0.0204 (6)	0.0236 (6)	0.0274 (6)	−0.0048 (4)	0.0009 (5)	−0.0001 (5)
N1	0.0190 (7)	0.0217 (7)	0.0228 (7)	−0.0020 (5)	0.0020 (6)	−0.0028 (5)
N2	0.0318 (9)	0.0269 (8)	0.0459 (10)	0.0004 (6)	0.0076 (7)	−0.0016 (7)
C1	0.0209 (8)	0.0221 (8)	0.0205 (7)	−0.0027 (6)	−0.0026 (6)	−0.0037 (6)
C2	0.0211 (8)	0.0206 (8)	0.0210 (7)	−0.0022 (6)	−0.0013 (6)	−0.0042 (6)
C3	0.0185 (8)	0.0262 (8)	0.0186 (7)	−0.0035 (6)	−0.0020 (6)	−0.0036 (6)
C4	0.0197 (8)	0.0230 (8)	0.0221 (7)	−0.0035 (6)	−0.0019 (6)	−0.0015 (6)
C5	0.0208 (8)	0.0229 (8)	0.0236 (8)	−0.0038 (6)	−0.0015 (7)	−0.0017 (6)
C6	0.0262 (9)	0.0206 (8)	0.0348 (9)	−0.0003 (6)	0.0036 (7)	−0.0008 (7)
C7	0.0218 (9)	0.0247 (9)	0.0241 (8)	−0.0025 (6)	0.0034 (7)	−0.0023 (6)
C8	0.0227 (8)	0.0205 (8)	0.0209 (8)	−0.0055 (6)	0.0015 (6)	−0.0035 (6)
C9	0.0283 (9)	0.0258 (8)	0.0223 (8)	−0.0028 (6)	−0.0016 (7)	−0.0022 (6)
C10	0.0380 (10)	0.0310 (9)	0.0200 (8)	−0.0087 (7)	0.0020 (7)	−0.0036 (7)
C11	0.0293 (10)	0.0279 (9)	0.0268 (8)	−0.0072 (7)	0.0100 (7)	−0.0093 (7)
C12	0.0236 (9)	0.0287 (9)	0.0337 (9)	−0.0031 (6)	0.0010 (7)	−0.0050 (7)
C13	0.0234 (9)	0.0295 (9)	0.0225 (8)	−0.0052 (6)	0.0000 (7)	−0.0044 (6)
C14	0.0225 (9)	0.0245 (8)	0.0257 (8)	−0.0036 (6)	0.0006 (7)	−0.0011 (6)
C15	0.0272 (9)	0.0279 (9)	0.0305 (9)	−0.0113 (7)	0.0037 (7)	0.0007 (7)
C16	0.0672 (16)	0.0527 (13)	0.0337 (11)	−0.0275 (12)	0.0154 (11)	−0.0070 (10)

Geometric parameters (Å, º)

Cl1—C11	1.7422 (17)	C6—H6B	0.9800
S1—C1	1.6814 (17)	C6—H6C	0.9800
O1—C14	1.204 (2)	C8—C13	1.395 (2)
O2—C14	1.331 (2)	C8—C9	1.395 (2)
O2—C15	1.4620 (19)	C9—C10	1.387 (3)
N1—C5	1.357 (2)	C9—H9	0.9500
N1—C1	1.367 (2)	C10—C11	1.385 (3)
N1—H1	0.9099	C10—H10	0.9500
N2—C7	1.146 (2)	C11—C12	1.383 (3)
C1—C2	1.420 (2)	C12—C13	1.389 (3)
C2—C3	1.390 (2)	C12—H12	0.9500
C2—C7	1.435 (2)	C13—H13	0.9500
C3—C4	1.415 (2)	C15—C16	1.494 (3)
C3—C8	1.491 (2)	C15—H15A	0.9900
C4—C5	1.384 (2)	C15—H15B	0.9900
C4—C14	1.502 (2)	C16—H16A	0.9800
C5—C6	1.492 (2)	C16—H16B	0.9800

C6—H6A	0.9800	C16—H16C	0.9800
C14—O2—C15	115.95 (13)	C10—C9—H9	119.9
C5—N1—C1	126.21 (14)	C8—C9—H9	119.9
C5—N1—H1	118.0	C11—C10—C9	119.25 (16)
C1—N1—H1	115.5	C11—C10—H10	120.4
N1—C1—C2	114.40 (14)	C9—C10—H10	120.4
N1—C1—S1	121.52 (13)	C12—C11—C10	121.55 (17)
C2—C1—S1	124.07 (12)	C12—C11—Cl1	119.24 (15)
C3—C2—C1	122.33 (14)	C10—C11—Cl1	119.20 (14)
C3—C2—C7	120.41 (15)	C11—C12—C13	118.94 (17)
C1—C2—C7	117.08 (14)	C11—C12—H12	120.5
C2—C3—C4	118.89 (14)	C13—C12—H12	120.5
C2—C3—C8	119.03 (14)	C12—C13—C8	120.49 (16)
C4—C3—C8	121.95 (14)	C12—C13—H13	119.8
C5—C4—C3	119.21 (15)	C8—C13—H13	119.8
C5—C4—C14	119.27 (14)	O1—C14—O2	124.50 (16)
C3—C4—C14	121.52 (14)	O1—C14—C4	123.73 (16)
N1—C5—C4	118.84 (15)	O2—C14—C4	111.76 (13)
N1—C5—C6	114.21 (14)	O2—C15—C16	110.94 (14)
C4—C5—C6	126.90 (15)	O2—C15—H15A	109.5
C5—C6—H6A	109.5	C16—C15—H15A	109.5
C5—C6—H6B	109.5	O2—C15—H15B	109.5
H6A—C6—H6B	109.5	C16—C15—H15B	109.5
C5—C6—H6C	109.5	H15A—C15—H15B	108.0
H6A—C6—H6C	109.5	C15—C16—H16A	109.5
H6B—C6—H6C	109.5	C15—C16—H16B	109.5
N2—C7—C2	179.0 (2)	H16A—C16—H16B	109.5
C13—C8—C9	119.50 (16)	C15—C16—H16C	109.5
C13—C8—C3	121.05 (14)	H16A—C16—H16C	109.5
C9—C8—C3	119.35 (15)	H16B—C16—H16C	109.5
C10—C9—C8	120.20 (17)		
C5—N1—C1—C2	0.7 (2)	C4—C3—C8—C13	−121.73 (17)
C5—N1—C1—S1	179.31 (12)	C2—C3—C8—C9	−114.02 (17)
N1—C1—C2—C3	2.4 (2)	C4—C3—C8—C9	61.9 (2)
S1—C1—C2—C3	−176.18 (12)	C13—C8—C9—C10	0.5 (2)
N1—C1—C2—C7	177.60 (14)	C3—C8—C9—C10	176.94 (15)
S1—C1—C2—C7	−1.0 (2)	C8—C9—C10—C11	1.8 (3)
C1—C2—C3—C4	−3.5 (2)	C9—C10—C11—C12	−2.7 (3)
C7—C2—C3—C4	−178.47 (14)	C9—C10—C11—Cl1	177.79 (13)
C1—C2—C3—C8	172.56 (14)	C10—C11—C12—C13	1.4 (3)
C7—C2—C3—C8	−2.4 (2)	Cl1—C11—C12—C13	−179.14 (13)
C2—C3—C4—C5	1.4 (2)	C11—C12—C13—C8	0.9 (3)
C8—C3—C4—C5	−174.47 (14)	C9—C8—C13—C12	−1.9 (2)
C2—C3—C4—C14	−178.12 (14)	C3—C8—C13—C12	−178.24 (15)
C8—C3—C4—C14	6.0 (2)	C15—O2—C14—O1	0.1 (2)
C1—N1—C5—C4	−2.6 (2)	C15—O2—C14—C4	179.63 (13)

C1—N1—C5—C6	174.96 (15)	C5—C4—C14—O1	47.2 (2)
C3—C4—C5—N1	1.4 (2)	C3—C4—C14—O1	−133.26 (19)
C14—C4—C5—N1	−179.01 (14)	C5—C4—C14—O2	−132.40 (16)
C3—C4—C5—C6	−175.77 (15)	C3—C4—C14—O2	47.2 (2)
C14—C4—C5—C6	3.8 (3)	C14—O2—C15—C16	88.8 (2)
C2—C3—C8—C13	62.4 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···S1^{i}	0.91	2.40	3.2911 (14)	166
C6—H6*A*···O1	0.98	2.36	3.047 (2)	127
C6—H6*B*···N2^{ii}	0.98	2.45	3.305 (2)	145
C15—H15*B*···O1^{iii}	0.99	2.41	3.327 (2)	153

Symmetry codes: (i) −*x*+3, −*y*+1, −*z*+1; (ii) *x*+1, *y*−1, *z*; (iii) *x*−1, *y*, *z*.