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5-(2-Cyanobenzyl)-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridin-2-yl acetate

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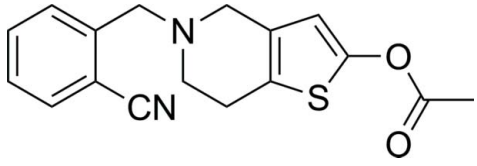
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.098; data-to-parameter ratio = 15.1.

In the title molecule, $C_{17}H_{16}N_2O_2S$, the tetrahydropyridine ring exhibits a half-chair conformation. The mean planes of the ester chain and benzene ring are twisted by 5.5 (1) and 81.32 (5)°, respectively, from the plane of thiophene ring. In the crystal, weak C—H···O interactions link molecules related by translation along [100] into chains.

Related literature

For the crystal structures of related compounds, see: Wang *et al.* (2010); Yang *et al.* (2012). For details of the synthesis, see: Zhou *et al.* (2011).



Experimental

Crystal data

$C_{17}H_{16}N_2O_2S$
M_r = 312.38
Monoclinic, $P2_1/n$
a = 14.174 (3) Å
b = 5.9321 (12) Å
c = 18.796 (4) Å
β = 99.06 (3)°
V = 1560.7 (5) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 1.91 mm^{-1}
T = 113 K
0.26 × 0.24 × 0.22 mm

Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
T_{min} = 0.636, T_{max} = 0.678
16000 measured reflections
3034 independent reflections
2819 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.098
S = 1.08
3034 reflections
201 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11···O2^{i}	0.95	2.53	3.3346 (19)	143

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

Data collection: *CrystalClear* (Rigaku/MSC, 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: *CrystalStructure* (Rigaku/MSC, 2005).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5399).

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supporting information

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5-(2-Cyanobenzyl)-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridin-2-yl acetate

Xiao-Shuai Xie, Shuai Mu, Ying Liu and Deng-Ke Liu

S1. Comment

As a continuation of our structural study of tetrahydrothienopyridine derivatives (Yang *et al.*, 2012), herein we present the crystal structure of the title compound (I).

In (I) (Fig. 1), all bond lengths and angles are normal and correspond to those observed in the related compounds 5-[(2-cyclopropylcarbonyl)(2- fluorophenyl)methyl]-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridin- 2-yl acetate (Prasugrel) (Wang *et al.*, 2010) and 5-(2-chlorobenzyl)-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridin-2-yl acetate (Yang *et al.*, 2012). The ester chain in (I) is almost planar with a mean deviation of 0.0021 Å. The tetrahydropyridine ring exhibits a half-chair conformation. The mean planes of the ester chain and benzene ring are twisted at 5.5 (1) and 81.32 (5)°, respectively, from the plane of thiophene ring. In the crystal, weak C—H···O interactions (Table 1) link the molecules related by translation in [100] into chains.

S2. Experimental

The title compound was prepared according to the method of Zhou *et al.* (2011). 19.2 g of 5,6,7,7a-tetrahydrothieno[3,2-*c*]pyridin-2(4*H*)-one hydrochloride and 29 g of *N*-methyl morpholine were dissolved in 100 ml of $CHCl_3$. 42.6 g of 2-(bromomethyl)benzonitrile was dropwised into the mixture and then refluxed for 4 h. After filtration, the resulting filtrate was evaporated under reduced pressure. The residue was dissolved in diethyl ether, adjust the pH=5 to get 2-{(2-oxo-7,7a-dihydrothieno [3,2-*c*]pyridin-5(2*H*,4*H*,6*H*)-yl)methyl} benzonitrile as an intermediate. The intermediate, together with 14.5 g of *N*-methyl morpholine and 10 g of acetic anhydride was dissolved in 150 ml of acetonitrile and stirred under 30°C for 2 h. The mixture was evaporated under reduced pressure and yellow oil was obtained. The oil was dissolved in $CHCl_3$, washed with saturated brines for 3 times. The crude product was purified by silica gel chromatography to give white powder. Colorless single crystals were grown from a methanol solution.

S3. Refinement

All H atoms were positioned geometrically and refined using a riding model, with d(C—H) = 0.95 - 0.99 Å, and U_{iso} (H) = 1.5 or 1.2 U_{eq}(C).

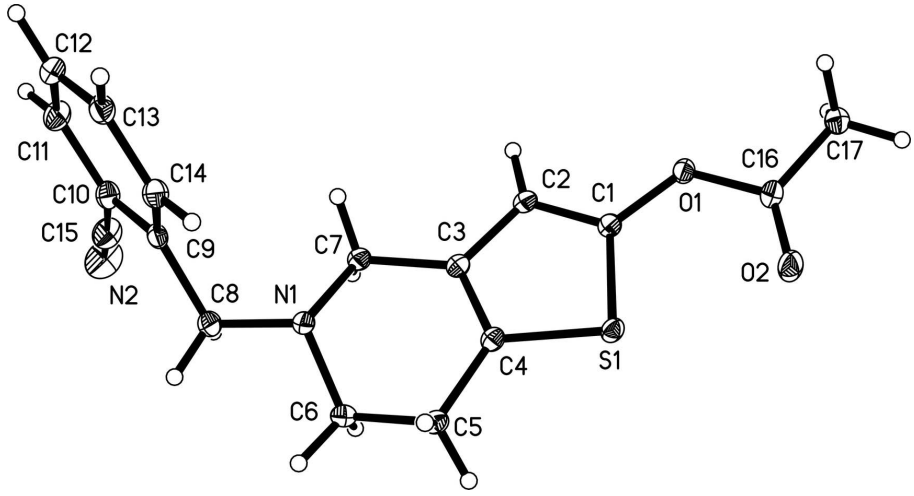

Figure 1

The molecular structure of (I) showing the atom-numbering scheme and 50% probability displacement ellipsoids.

5-(2-Cyanobenzyl)-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridin-2-yl acetate

Crystal data

$C_{17}H_{16}N_2O_2S$
$M_r = 312.38$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 14.174\ (3)$ Å
$b = 5.9321\ (12)$ Å
$c = 18.796\ (4)$ Å
$\beta = 99.06\ (3)°$
$V = 1560.7\ (5)$ Å^3
$Z = 4$
$F(000) = 656$
$D_x = 1.329$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54187$ Å
Cell parameters from 2001 reflections
$\theta = 27.6–72.2°$
$\mu = 1.91$ mm^{-1}
$T = 113$ K
Prism, colourless
0.26 × 0.24 × 0.22 mm

Data collection

Rigaku Saturn diffractometer
Radiation source: fine-focus sealed tube
Multilayer monochromator
Detector resolution: 14.63 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
$T_{min} = 0.636$, $T_{max} = 0.678$
16000 measured reflections
3034 independent reflections
2819 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$
$\theta_{max} = 72.5°$, $\theta_{min} = 3.6°$
$h = -17\rightarrow17$
$k = -7\rightarrow7$
$l = -17\rightarrow23$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.098$
$S = 1.08$
3034 reflections
201 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2 + 0.3535P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0040 (4)

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	0.07455 (2)	0.16825 (5)	0.143145 (17)	0.02086 (13)
O1	0.02603 (6)	−0.21422 (16)	0.06058 (5)	0.0237 (2)
O2	−0.09148 (7)	−0.05922 (19)	0.11147 (6)	0.0356 (3)
N1	0.38740 (7)	0.30018 (18)	0.16585 (6)	0.0202 (3)
N2	0.64150 (12)	0.3514 (3)	0.02028 (9)	0.0527 (4)
C1	0.09324 (9)	−0.0540 (2)	0.08710 (7)	0.0201 (3)
C2	0.18393 (9)	−0.0624 (2)	0.07280 (7)	0.0201 (3)
H2	0.2064	−0.1715	0.0425	0.024*
C3	0.24163 (9)	0.1132 (2)	0.10896 (7)	0.0187 (3)
C4	0.19251 (9)	0.2503 (2)	0.14809 (7)	0.0196 (3)
C5	0.23440 (9)	0.4496 (2)	0.19049 (7)	0.0216 (3)
H5A	0.2447	0.4142	0.2426	0.026*
H5B	0.1904	0.5799	0.1820	0.026*
C6	0.32936 (9)	0.5055 (2)	0.16606 (7)	0.0217 (3)
H6A	0.3175	0.5712	0.1170	0.026*
H6B	0.3643	0.6183	0.1990	0.026*
C7	0.34597 (9)	0.1510 (2)	0.10650 (7)	0.0206 (3)
H7A	0.3800	0.0047	0.1106	0.025*
H7B	0.3537	0.2201	0.0598	0.025*
C8	0.48585 (9)	0.3588 (2)	0.15919 (8)	0.0245 (3)
H8A	0.5078	0.4827	0.1931	0.029*
H8B	0.4879	0.4140	0.1097	0.029*
C9	0.55298 (9)	0.1608 (2)	0.17475 (7)	0.0207 (3)
C10	0.62212 (9)	0.1119 (2)	0.13184 (8)	0.0255 (3)
C11	0.68601 (10)	−0.0673 (3)	0.14838 (9)	0.0321 (3)
H11	0.7327	−0.0980	0.1185	0.038*
C12	0.68115 (10)	−0.1995 (2)	0.20814 (9)	0.0311 (3)
H12	0.7242	−0.3218	0.2195	0.037*
C13	0.61310 (10)	−0.1526 (2)	0.25154 (8)	0.0276 (3)
H13	0.6097	−0.2425	0.2929	0.033*
C14	0.54986 (9)	0.0252 (2)	0.23487 (8)	0.0250 (3)
H14	0.5035	0.0551	0.2651	0.030*
C15	0.63104 (11)	0.2481 (3)	0.06926 (9)	0.0351 (4)

C16	−0.06452 (9)	−0.2078 (2)	0.07641 (8)	0.0233 (3)
C17	−0.12011 (10)	−0.4073 (2)	0.04513 (8)	0.0270 (3)
H17A	−0.1192	−0.4134	−0.0069	0.040*
H17B	−0.1862	−0.3947	0.0539	0.040*
H17C	−0.0914	−0.5451	0.0678	0.040*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01803 (19)	0.0246 (2)	0.0204 (2)	0.00246 (11)	0.00426 (13)	−0.00427 (11)
O1	0.0176 (5)	0.0254 (5)	0.0282 (5)	−0.0002 (4)	0.0038 (4)	−0.0072 (4)
O2	0.0237 (5)	0.0417 (6)	0.0437 (7)	−0.0034 (4)	0.0123 (5)	−0.0190 (5)
N1	0.0178 (5)	0.0186 (5)	0.0246 (6)	0.0000 (4)	0.0041 (4)	0.0001 (4)
N2	0.0543 (10)	0.0658 (11)	0.0433 (9)	0.0074 (8)	0.0242 (8)	0.0159 (8)
C1	0.0199 (6)	0.0217 (6)	0.0185 (6)	0.0014 (5)	0.0017 (5)	−0.0015 (5)
C2	0.0205 (6)	0.0205 (6)	0.0191 (6)	0.0041 (5)	0.0028 (5)	−0.0012 (5)
C3	0.0197 (6)	0.0200 (6)	0.0163 (6)	0.0024 (5)	0.0025 (5)	0.0022 (5)
C4	0.0191 (6)	0.0221 (6)	0.0174 (6)	0.0026 (5)	0.0028 (5)	0.0005 (5)
C5	0.0225 (6)	0.0216 (6)	0.0209 (7)	0.0025 (5)	0.0046 (5)	−0.0020 (5)
C6	0.0250 (6)	0.0179 (6)	0.0225 (7)	0.0009 (5)	0.0050 (5)	−0.0001 (5)
C7	0.0202 (6)	0.0202 (6)	0.0219 (7)	0.0014 (5)	0.0051 (5)	−0.0013 (5)
C8	0.0207 (6)	0.0224 (6)	0.0310 (8)	−0.0028 (5)	0.0063 (5)	0.0020 (5)
C9	0.0167 (6)	0.0218 (6)	0.0234 (7)	−0.0039 (5)	0.0020 (5)	−0.0015 (5)
C10	0.0214 (6)	0.0303 (7)	0.0255 (7)	−0.0028 (5)	0.0059 (5)	−0.0009 (6)
C11	0.0236 (7)	0.0369 (8)	0.0376 (9)	0.0032 (6)	0.0103 (6)	−0.0024 (7)
C12	0.0217 (7)	0.0268 (7)	0.0433 (9)	0.0026 (5)	0.0009 (6)	0.0013 (6)
C13	0.0242 (7)	0.0268 (7)	0.0303 (8)	−0.0040 (5)	0.0003 (6)	0.0052 (6)
C14	0.0226 (6)	0.0275 (7)	0.0257 (7)	−0.0023 (5)	0.0058 (5)	0.0011 (6)
C15	0.0322 (8)	0.0425 (9)	0.0337 (8)	0.0026 (7)	0.0152 (7)	0.0033 (7)
C16	0.0182 (6)	0.0285 (7)	0.0231 (7)	0.0011 (5)	0.0028 (5)	−0.0003 (5)
C17	0.0229 (7)	0.0270 (7)	0.0306 (8)	−0.0010 (5)	0.0029 (6)	−0.0025 (6)

Geometric parameters (Å, º)

S1—C4	1.7297 (13)	C7—H7A	0.9900
S1—C1	1.7338 (13)	C7—H7B	0.9900
O1—C16	1.3629 (16)	C8—C9	1.5109 (18)
O1—C1	1.3819 (16)	C8—H8A	0.9900
O2—C16	1.1987 (17)	C8—H8B	0.9900
N1—C8	1.4625 (16)	C9—C14	1.393 (2)
N1—C6	1.4702 (16)	C9—C10	1.394 (2)
N1—C7	1.4716 (17)	C10—C11	1.399 (2)
N2—C15	1.135 (2)	C10—C15	1.449 (2)
C1—C2	1.3549 (18)	C11—C12	1.381 (2)
C2—C3	1.4284 (18)	C11—H11	0.9500
C2—H2	0.9500	C12—C13	1.386 (2)
C3—C4	1.3594 (18)	C12—H12	0.9500
C3—C7	1.5037 (17)	C13—C14	1.388 (2)

C4—C5	1.4955 (18)	C13—H13	0.9500
C5—C6	1.5256 (18)	C14—H14	0.9500
C5—H5A	0.9900	C16—C17	1.4905 (19)
C5—H5B	0.9900	C17—H17A	0.9800
C6—H6A	0.9900	C17—H17B	0.9800
C6—H6B	0.9900	C17—H17C	0.9800

C4—S1—C1	90.43 (6)	N1—C8—C9	112.25 (10)
C16—O1—C1	121.43 (10)	N1—C8—H8A	109.2
C8—N1—C6	110.18 (10)	C9—C8—H8A	109.2
C8—N1—C7	110.52 (10)	N1—C8—H8B	109.2
C6—N1—C7	110.09 (10)	C9—C8—H8B	109.2
C2—C1—O1	121.66 (11)	H8A—C8—H8B	107.9
C2—C1—S1	112.89 (10)	C14—C9—C10	117.63 (12)
O1—C1—S1	125.42 (9)	C14—C9—C8	120.42 (12)
C1—C2—C3	111.65 (11)	C10—C9—C8	121.90 (12)
C1—C2—H2	124.2	C9—C10—C11	121.26 (13)
C3—C2—H2	124.2	C9—C10—C15	120.83 (13)
C4—C3—C2	112.94 (11)	C11—C10—C15	117.90 (13)
C4—C3—C7	121.15 (12)	C12—C11—C10	119.92 (13)
C2—C3—C7	125.90 (11)	C12—C11—H11	120.0
C3—C4—C5	124.54 (12)	C10—C11—H11	120.0
C3—C4—S1	112.08 (10)	C11—C12—C13	119.56 (14)
C5—C4—S1	123.38 (9)	C11—C12—H12	120.2
C4—C5—C6	107.86 (10)	C13—C12—H12	120.2
C4—C5—H5A	110.1	C12—C13—C14	120.29 (14)
C6—C5—H5A	110.1	C12—C13—H13	119.9
C4—C5—H5B	110.1	C14—C13—H13	119.9
C6—C5—H5B	110.1	C13—C14—C9	121.34 (13)
H5A—C5—H5B	108.4	C13—C14—H14	119.3
N1—C6—C5	109.95 (10)	C9—C14—H14	119.3
N1—C6—H6A	109.7	N2—C15—C10	177.32 (17)
C5—C6—H6A	109.7	O2—C16—O1	122.22 (12)
N1—C6—H6B	109.7	O2—C16—C17	127.33 (12)
C5—C6—H6B	109.7	O1—C16—C17	110.45 (11)
H6A—C6—H6B	108.2	C16—C17—H17A	109.5
N1—C7—C3	110.09 (10)	C16—C17—H17B	109.5
N1—C7—H7A	109.6	H17A—C17—H17B	109.5
C3—C7—H7A	109.6	C16—C17—H17C	109.5
N1—C7—H7B	109.6	H17A—C17—H17C	109.5
C3—C7—H7B	109.6	H17B—C17—H17C	109.5
H7A—C7—H7B	108.2		

C16—O1—C1—C2	178.55 (12)	C4—C3—C7—N1	16.65 (17)
C16—O1—C1—S1	0.90 (18)	C2—C3—C7—N1	−163.09 (12)
C4—S1—C1—C2	−0.56 (11)	C6—N1—C8—C9	167.62 (11)
C4—S1—C1—O1	177.27 (12)	C7—N1—C8—C9	−70.50 (14)
O1—C1—C2—C3	−176.86 (11)	N1—C8—C9—C14	−46.34 (17)

S1—C1—C2—C3	1.06 (14)	N1—C8—C9—C10	136.16 (13)
C1—C2—C3—C4	−1.16 (16)	C14—C9—C10—C11	0.2 (2)
C1—C2—C3—C7	178.60 (12)	C8—C9—C10—C11	177.72 (13)
C2—C3—C4—C5	−179.07 (12)	C14—C9—C10—C15	−178.76 (13)
C7—C3—C4—C5	1.2 (2)	C8—C9—C10—C15	−1.2 (2)
C2—C3—C4—S1	0.74 (15)	C9—C10—C11—C12	0.0 (2)
C7—C3—C4—S1	−179.03 (10)	C15—C10—C11—C12	178.99 (14)
C1—S1—C4—C3	−0.12 (11)	C10—C11—C12—C13	−0.3 (2)
C1—S1—C4—C5	179.69 (11)	C11—C12—C13—C14	0.4 (2)
C3—C4—C5—C6	14.85 (18)	C12—C13—C14—C9	−0.2 (2)
S1—C4—C5—C6	−164.94 (10)	C10—C9—C14—C13	−0.1 (2)
C8—N1—C6—C5	−166.73 (11)	C8—C9—C14—C13	−177.70 (12)
C7—N1—C6—C5	71.13 (13)	C9—C10—C15—N2	162 (4)
C4—C5—C6—N1	−49.11 (14)	C11—C10—C15—N2	−17 (4)
C8—N1—C7—C3	−173.55 (10)	C1—O1—C16—O2	3.0 (2)
C6—N1—C7—C3	−51.61 (13)	C1—O1—C16—C17	−176.31 (11)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···O2^{i}	0.95	2.53	3.3346 (19)	143

Symmetry code: (i) *x*+1, *y*, *z*.