

Ethyl 2-acetylamino-4,5,6,7-tetrahydro-1-benzothiophene-3-carboxylate

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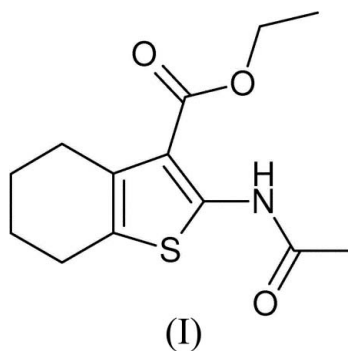
Key indicators

Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.036
 wR factor = 0.091
Data-to-parameter ratio = 17.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The geometrical parameters for the title compound, $\text{C}_{13}\text{H}_{17}\text{NO}_3\text{S}$, are normal. The planar molecular conformation is reinforced by an intramolecular $\text{N}-\text{H}\cdots\text{O}$ interaction.

Comment

Thiophene derivatives are known to exhibit an array of biological effects, including analgesic and anti-inflammatory activities (Ramanathan & Namboothiri, 1978; Cannito *et al.*, 1990). As part of our own research in this area, the structure of the title compound, (I) (Fig. 1), is presented.



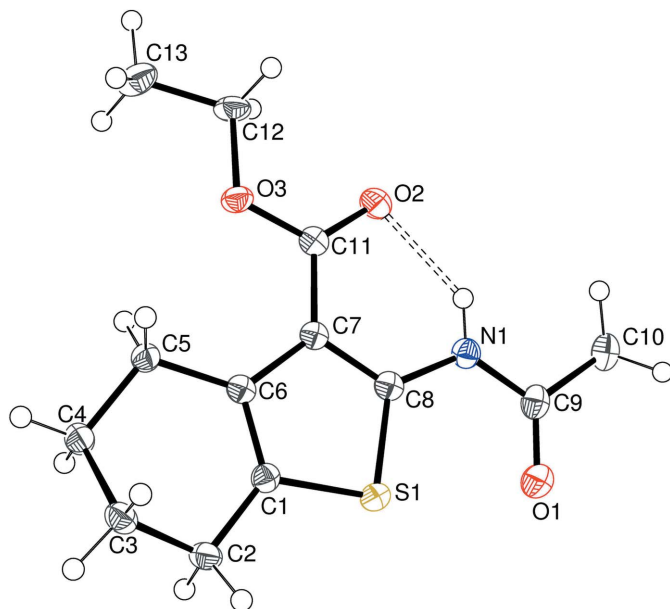
The geometric parameters for (I) are normal. The five-membered C1/C2/C6/C7/S1 ring is almost planar (r.m.s. deviation from the mean plane = 0.013 Å). The C1–C6 ring is in a half-chair conformation (Table 1), with atoms C1, C2, C5 and C6 almost co-planar (r.m.s. deviation = 0.003 Å) and atoms C3 and C4 displaced from this plane by -0.480 (3) and 0.277 (3) Å, respectively. An intramolecular $\text{N}-\text{H}\cdots\text{O}$ bond (Table 2) helps to establish the molecular conformation. Overall, the molecule of (I) is approximately planar.

The molecular packing for (I) comprises undulating sheets lying parallel to the $(10\bar{1})$ plane (Fig. 2). Within these sheets, the shortest intermolecular contacts are $\text{C}-\text{H}\cdots\text{O}$ interactions (Table 2).

Experimental

Ethyl-2-amino-4,5,6,7-tetrahydro-1-benzothiophene-3-carboxylate, (II), was prepared from cyclohexanone, sulfur and ethyl cyanoacetate by a one-pot thiolation-heterocyclization reaction (Gewald *et al.*, 1966). A mixture of (II) (3.5 g, 0.015 mol), acetic anhydride (14 ml) and zinc dust (0.883 g, 0.015 mol) was refluxed for 2 h. The reaction mixture was cooled to room temperature and the solid product was recovered. The crude product was dissolved in warm (318 K) methanol (35 ml) and filtered. The product was recrystallized from acetone to yield colourless crystals of (I) (yield 84.3%; m.p. 388 K). IR (KBr, cm^{-1}): 3436 and 3244 ($-\text{NH}-$), 2931 and 2873 ($-\text{CH}-$),

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**Figure 1**

The molecular structure of (I), showing 50% probability displacement ellipsoids and arbitrary spheres for the H atoms. The intramolecular hydrogen bond is indicated by a dashed line.

1666 and 1546 (C=O) and 1250 (C—O). Elemental analysis, found: C 58.18, H 6.32, N 5.16%; calculated: C 58.40, H 6.41, N 5.24%.

Crystal data

$C_{13}H_{17}NO_3S$
 $M_r = 267.34$
 Monoclinic, $P2_1/c$
 $a = 10.2987$ (4) Å
 $b = 16.6174$ (5) Å
 $c = 7.8510$ (3) Å
 $\beta = 108.4381$ (18)°
 $V = 1274.63$ (8) Å³

$Z = 4$
 $D_x = 1.393$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.25$ mm⁻¹
 $T = 120$ (2) K
 Cut block, colourless
 $0.44 \times 0.30 \times 0.18$ mm

Data collection

Nonius KappaCCD diffractometer
 ω and φ scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2003)
 $T_{\min} = 0.897$, $T_{\max} = 0.958$

16538 measured reflections
 2917 independent reflections
 2338 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$
 $\theta_{\max} = 27.5^\circ$

Refinement

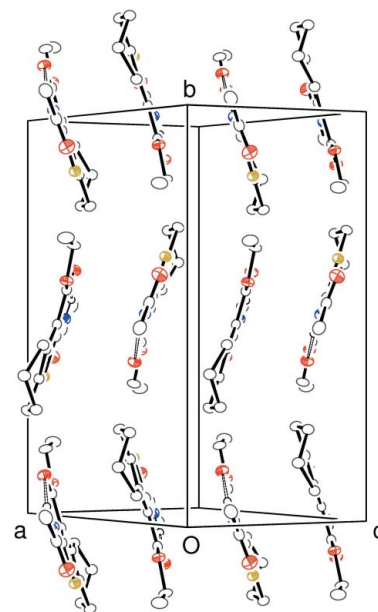
Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.091$
 $S = 1.05$
 2917 reflections
 168 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.574P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.28$ e Å⁻³
 $\Delta\rho_{\min} = -0.28$ e Å⁻³

Table 1

Selected torsion angles (°).

C1—C2—C3—C4	48.83 (16)	C4—C5—C6—C1	−10.54 (19)
C2—C3—C4—C5	−63.48 (17)	C5—C6—C1—C2	−0.9 (2)
C3—C4—C5—C6	42.28 (18)	C6—C1—C2—C3	−18.7 (2)

**Figure 2**

A view of the unit-cell contents of (I), with H atoms (except H1) omitted for clarity.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O2	0.858 (18)	1.979 (18)	2.6798 (17)	138.1 (16)
C2—H2A \cdots O2 ⁱ	0.99	2.44	3.370 (2)	157

Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.

The N-bound H atom was located in a difference map and its position was refined freely, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. The C-bound H atoms were placed in idealised locations (C—H = 0.98–0.99 Å) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$. The methyl groups were allowed to rotate about their local threefold axes to fit the electron density.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997) and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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supporting information

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$\beta = 108.4381\ (18)^\circ$

$V = 1274.63\ (8)\ \text{\AA}^3$

$Z = 4$

$F(000) = 568$

$D_x = 1.393\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3015 reflections

$\theta = 1.0\text{--}27.5^\circ$

$\mu = 0.25\ \text{mm}^{-1}$

$T = 120\ \text{K}$

Cut block, colourless

$0.44 \times 0.30 \times 0.18\ \text{mm}$

Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and ϕ scans

Absorption correction: multi-scan

(SADABS; Bruker, 2003)

$T_{\min} = 0.897$, $T_{\max} = 0.958$

16538 measured reflections

2917 independent reflections

2338 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.2^\circ$

$h = -13 \rightarrow 13$

$k = -21 \rightarrow 20$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.091$

$S = 1.05$

2917 reflections

168 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 atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.574P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.28\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.28\ \text{e \AA}^{-3}$

Special details

Experimental. IR (KBr, cm^{-1}): 3436 and 3244 (—NH—), 2931 and 2873 (—CH—), 1666 and 1546 (C=O) and 1250 (C—O). Elemental analysis, found: C 58.18, H 6.32, N 5.16%; calculated: C 58.40, H 6.41, N 5.24%.

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.42025 (15)	0.34938 (9)	0.5719 (2)	0.0190 (3)
C2	0.36910 (16)	0.27403 (9)	0.4663 (2)	0.0232 (3)
H2A	0.3934	0.2266	0.5464	0.028*
H2B	0.4126	0.2679	0.3712	0.028*
C3	0.21396 (16)	0.27903 (9)	0.3819 (2)	0.0232 (3)
H3A	0.1817	0.2347	0.2944	0.028*
H3B	0.1696	0.2731	0.4762	0.028*
C4	0.17450 (16)	0.35977 (9)	0.2872 (2)	0.0229 (3)
H4A	0.0746	0.3605	0.2246	0.028*
H4B	0.2214	0.3658	0.1956	0.028*
C5	0.21240 (15)	0.43102 (9)	0.41786 (19)	0.0194 (3)
H5A	0.2108	0.4812	0.3493	0.023*
H5B	0.1433	0.4362	0.4808	0.023*
C6	0.35228 (15)	0.42071 (9)	0.55453 (19)	0.0178 (3)
C7	0.43107 (14)	0.48049 (9)	0.67846 (19)	0.0175 (3)
C8	0.55668 (15)	0.45085 (9)	0.78253 (19)	0.0189 (3)
C9	0.78203 (16)	0.46767 (10)	1.0084 (2)	0.0232 (3)
C10	0.86975 (16)	0.52769 (10)	1.1382 (2)	0.0276 (4)
H10A	0.8119	0.5710	1.1592	0.041*
H10B	0.9375	0.5504	1.0878	0.041*
H10C	0.9169	0.5008	1.2521	0.041*
C11	0.39415 (15)	0.56423 (9)	0.6996 (2)	0.0191 (3)
C12	0.23372 (17)	0.66948 (9)	0.5971 (2)	0.0261 (4)
H12A	0.3078	0.7041	0.5829	0.031*
H12B	0.2198	0.6825	0.7131	0.031*
C13	0.10391 (17)	0.68309 (10)	0.4450 (3)	0.0323 (4)
H13A	0.0775	0.7398	0.4423	0.048*
H13B	0.0309	0.6494	0.4621	0.048*
H13C	0.1186	0.6689	0.3313	0.048*
N1	0.65371 (13)	0.49412 (8)	0.91396 (17)	0.0208 (3)
H1	0.6261 (17)	0.5419 (11)	0.925 (2)	0.025*
O1	0.82149 (11)	0.40043 (7)	0.98601 (16)	0.0315 (3)
O2	0.46870 (11)	0.61218 (6)	0.80471 (15)	0.0253 (3)

O3	0.26963 (11)	0.58460 (6)	0.59197 (14)	0.0220 (2)
S1	0.58051 (4)	0.35234 (2)	0.73354 (5)	0.02108 (12)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0201 (7)	0.0197 (7)	0.0179 (7)	0.0006 (6)	0.0067 (6)	0.0014 (6)
C2	0.0301 (8)	0.0172 (8)	0.0221 (8)	0.0028 (6)	0.0077 (6)	−0.0015 (6)
C3	0.0293 (8)	0.0183 (8)	0.0211 (7)	−0.0028 (6)	0.0068 (6)	−0.0020 (6)
C4	0.0257 (8)	0.0202 (8)	0.0205 (8)	−0.0008 (6)	0.0038 (6)	−0.0008 (6)
C5	0.0199 (7)	0.0177 (7)	0.0195 (7)	0.0006 (6)	0.0048 (6)	0.0009 (6)
C6	0.0213 (7)	0.0178 (7)	0.0161 (7)	−0.0009 (6)	0.0087 (6)	0.0012 (6)
C7	0.0187 (7)	0.0185 (7)	0.0170 (7)	−0.0008 (6)	0.0082 (6)	0.0010 (6)
C8	0.0214 (7)	0.0193 (7)	0.0180 (7)	−0.0010 (6)	0.0092 (6)	0.0016 (6)
C9	0.0212 (8)	0.0291 (9)	0.0199 (7)	−0.0011 (6)	0.0072 (6)	0.0039 (7)
C10	0.0228 (8)	0.0335 (9)	0.0232 (8)	−0.0022 (7)	0.0025 (6)	0.0028 (7)
C11	0.0200 (7)	0.0196 (7)	0.0194 (7)	−0.0020 (6)	0.0088 (6)	0.0003 (6)
C12	0.0299 (9)	0.0138 (7)	0.0353 (9)	0.0028 (6)	0.0114 (7)	−0.0025 (7)
C13	0.0251 (9)	0.0219 (8)	0.0483 (11)	0.0033 (7)	0.0094 (8)	0.0038 (8)
N1	0.0194 (6)	0.0211 (7)	0.0213 (6)	−0.0016 (5)	0.0056 (5)	−0.0002 (5)
O1	0.0251 (6)	0.0326 (7)	0.0322 (7)	0.0046 (5)	0.0024 (5)	−0.0019 (5)
O2	0.0264 (6)	0.0203 (6)	0.0274 (6)	−0.0029 (5)	0.0057 (5)	−0.0048 (5)
O3	0.0213 (5)	0.0155 (5)	0.0279 (6)	0.0020 (4)	0.0061 (4)	−0.0008 (4)
S1	0.0205 (2)	0.0197 (2)	0.0226 (2)	0.00291 (15)	0.00611 (14)	0.00109 (15)

Geometric parameters (\AA , $^\circ$)

C1—C6	1.361 (2)	C8—N1	1.3884 (19)
C1—C2	1.502 (2)	C8—S1	1.7170 (15)
C1—S1	1.7356 (15)	C9—O1	1.221 (2)
C2—C3	1.526 (2)	C9—N1	1.3674 (19)
C2—H2A	0.990	C9—C10	1.505 (2)
C2—H2B	0.990	C10—H10A	0.980
C3—C4	1.525 (2)	C10—H10B	0.980
C3—H3A	0.990	C10—H10C	0.980
C3—H3B	0.990	C11—O2	1.2266 (18)
C4—C5	1.534 (2)	C11—O3	1.3370 (18)
C4—H4A	0.990	C12—O3	1.4619 (17)
C4—H4B	0.990	C12—C13	1.502 (2)
C5—C6	1.509 (2)	C12—H12A	0.990
C5—H5A	0.990	C12—H12B	0.990
C5—H5B	0.990	C13—H13A	0.980
C6—C7	1.446 (2)	C13—H13B	0.980
C7—C8	1.384 (2)	C13—H13C	0.980
C7—C11	1.466 (2)	N1—H1	0.858 (18)
C6—C1—C2	126.24 (14)	C7—C8—N1	124.98 (14)
C6—C1—S1	112.86 (11)	C7—C8—S1	112.34 (11)

C2—C1—S1	120.90 (11)	N1—C8—S1	122.68 (11)
C1—C2—C3	109.31 (12)	O1—C9—N1	121.65 (15)
C1—C2—H2A	109.8	O1—C9—C10	123.24 (14)
C3—C2—H2A	109.8	N1—C9—C10	115.11 (14)
C1—C2—H2B	109.8	C9—C10—H10A	109.5
C3—C2—H2B	109.8	C9—C10—H10B	109.5
H2A—C2—H2B	108.3	H10A—C10—H10B	109.5
C4—C3—C2	109.91 (13)	C9—C10—H10C	109.5
C4—C3—H3A	109.7	H10A—C10—H10C	109.5
C2—C3—H3A	109.7	H10B—C10—H10C	109.5
C4—C3—H3B	109.7	O2—C11—O3	122.13 (14)
C2—C3—H3B	109.7	O2—C11—C7	124.28 (14)
H3A—C3—H3B	108.2	O3—C11—C7	113.59 (12)
C3—C4—C5	112.40 (12)	O3—C12—C13	107.03 (13)
C3—C4—H4A	109.1	O3—C12—H12A	110.3
C5—C4—H4A	109.1	C13—C12—H12A	110.3
C3—C4—H4B	109.1	O3—C12—H12B	110.3
C5—C4—H4B	109.1	C13—C12—H12B	110.3
H4A—C4—H4B	107.9	H12A—C12—H12B	108.6
C6—C5—C4	111.81 (12)	C12—C13—H13A	109.5
C6—C5—H5A	109.3	C12—C13—H13B	109.5
C4—C5—H5A	109.3	H13A—C13—H13B	109.5
C6—C5—H5B	109.3	C12—C13—H13C	109.5
C4—C5—H5B	109.3	H13A—C13—H13C	109.5
H5A—C5—H5B	107.9	H13B—C13—H13C	109.5
C1—C6—C7	111.67 (13)	C9—N1—C8	125.56 (14)
C1—C6—C5	120.99 (13)	C9—N1—H1	122.4 (12)
C7—C6—C5	127.33 (13)	C8—N1—H1	111.9 (12)
C8—C7—C6	111.94 (13)	C11—O3—C12	115.31 (12)
C8—C7—C11	119.90 (13)	C8—S1—C1	91.18 (7)
C6—C7—C11	128.15 (13)		
C1—C2—C3—C4	48.83 (16)	C6—C7—C8—S1	−0.19 (16)
C2—C3—C4—C5	−63.48 (17)	C11—C7—C8—S1	−178.84 (11)
C3—C4—C5—C6	42.28 (18)	C8—C7—C11—O2	0.7 (2)
C4—C5—C6—C1	−10.54 (19)	C6—C7—C11—O2	−177.70 (14)
C5—C6—C1—C2	−0.9 (2)	C8—C7—C11—O3	−179.44 (12)
C6—C1—C2—C3	−18.7 (2)	C6—C7—C11—O3	2.1 (2)
S1—C1—C2—C3	161.76 (11)	O1—C9—N1—C8	−1.7 (2)
C2—C1—C6—C7	179.52 (14)	C10—C9—N1—C8	177.50 (13)
S1—C1—C6—C7	−0.95 (16)	C7—C8—N1—C9	−174.86 (14)
S1—C1—C6—C5	178.59 (11)	S1—C8—N1—C9	5.9 (2)
C4—C5—C6—C7	168.93 (14)	O2—C11—O3—C12	5.2 (2)
C1—C6—C7—C8	0.73 (18)	C7—C11—O3—C12	−174.69 (12)
C5—C6—C7—C8	−178.78 (13)	C13—C12—O3—C11	169.63 (13)
C1—C6—C7—C11	179.25 (14)	C7—C8—S1—C1	−0.29 (12)
C5—C6—C7—C11	−0.3 (2)	N1—C8—S1—C1	179.02 (13)
C6—C7—C8—N1	−179.48 (13)	C6—C1—S1—C8	0.73 (12)

C11—C7—C8—N1	1.9 (2)	C2—C1—S1—C8	−179.71 (13)
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Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots O2	0.858 (18)	1.979 (18)	2.6798 (17)	138.1 (16)
C2—H2 <i>A</i> \cdots O2 ⁱ	0.99	2.44	3.370 (2)	157

Symmetry code: (i) $-x+1, y-1/2, -z+3/2$.