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Ethyl 2-amino-4-phenyl-4*H*-1-benzo-thieno[3,2-*b*]pyran-3-carboxylateAdil Boughaleb,^a Hafid Zouihri,^b Said Gmouh,^c Abdelali Kerbal^a and Mohamed El yazidi^{a*}

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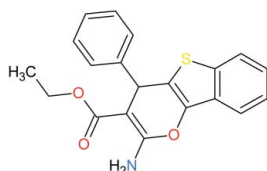
Received 14 June 2011; accepted 6 July 2011

Key indicators: single-crystal X-ray study; $T = 296$ K, $P = 0.0$ kPa; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.034; wR factor = 0.086; data-to-parameter ratio = 15.5.

The title heterocyclic compound, $\text{C}_{20}\text{H}_{17}\text{NO}_3\text{S}$, was synthesized by condensation of ethyl cyanoacetate with (*Z*)-2-benzylidenebenzo[*b*]thiophen-3(*2H*)-one in the presence of a basic catalyst in ethanol. The phenyl and ester groups make dihedral angles of 77.67 (6) and 8.52 (6)°, respectively, with the benzothienopyran ring system [maximum r.m.s. deviation = 0.1177 (13) Å]. In the crystal, centrosymmetric dimers are formed through pairs of $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds between the amine and ester groups. Intermolecular $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds and $\text{C}-\text{H}\cdots\pi$ interactions involving the thiophene ring are also observed.

Related literature

For general background to Michael addition reactions, see: Perlmutter (1992); Czarnocki *et al.* (2005); Rossiter & Swingle (1992).



Experimental

Crystal data

 $\text{C}_{20}\text{H}_{17}\text{NO}_3\text{S}$ $M_r = 351.41$

Monoclinic, $P2_1/n$
 $a = 8.6612$ (3) Å
 $b = 5.9156$ (2) Å
 $c = 32.3008$ (10) Å
 $\beta = 94.962$ (2)°
 $V = 1648.77$ (9) Å³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.22$ mm⁻¹
 $T = 296$ K
 $0.25 \times 0.14 \times 0.12$ mm

Data collection

Bruker APEXII CCD detector
diffractometer
21683 measured reflections

3608 independent reflections
3189 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.086$
 $S = 1.04$
3608 reflections
233 parameters
2 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.30$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the thiophene ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1B}\cdots\text{O2}^i$	0.838 (19)	2.285 (19)	2.9143 (16)	132.1 (15)
$\text{C10}-\text{H10}\cdots\text{N1}^{\text{ii}}$	0.98	2.57	3.5189 (17)	164
$\text{C15}-\text{H15}\cdots\text{Cg1}^{\text{iii}}$	0.93	2.95	3.7493 (15)	145

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

The authors thank the Unit of Support for Technical and Scientific Research (UATRS, CNRST) for the X-ray measurements.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2365).

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supporting information

Acta Cryst. (2011). E67, o2106 [doi:10.1107/S1600536811027152]

Ethyl 2-amino-4-phenyl-4*H*-1-benzothieno[3,2-*b*]pyran-3-carboxylate

Adil Boughaleb, Hafid Zouihri, Said Gmouh, Abdelali Kerbal and Mohamed El yazidi

S1. Comment

The Michael addition of carbanions to the C=C double bond of α,β -unsaturated ketones, nitriles, amides and esters is a method of choice for the formation of C—C bonds (Czarnocki *et al.*, 2005; Rossiter & Swingle, 1992; Perlmutter, 1992).

In this work we have studied the behavior of ethylcyanoacetate with respect to (*Z*)-2-benzylidenebenzo[*b*]thiophen-3(2*H*)-one and derivatives in ethanol, with the presence of piperidine as catalyst. We have shown that cyclocondensation starts with a Michael 1,4-addition, followed by intramolecular cyclization *via* nucleophilic addition of the hydroxyl group to the cyano group and not onto the carboxylate, to give the tricyclic heterocycle ethyl 2-amino-4-phenyl-4*H*-[1] benzothieno[3,2-*b*]pyran-3-carboxylate. The structural study by X-ray diffraction is in perfect agreement with the results of spectroscopic analysis: IR, ¹H- and ¹³C-NMR.

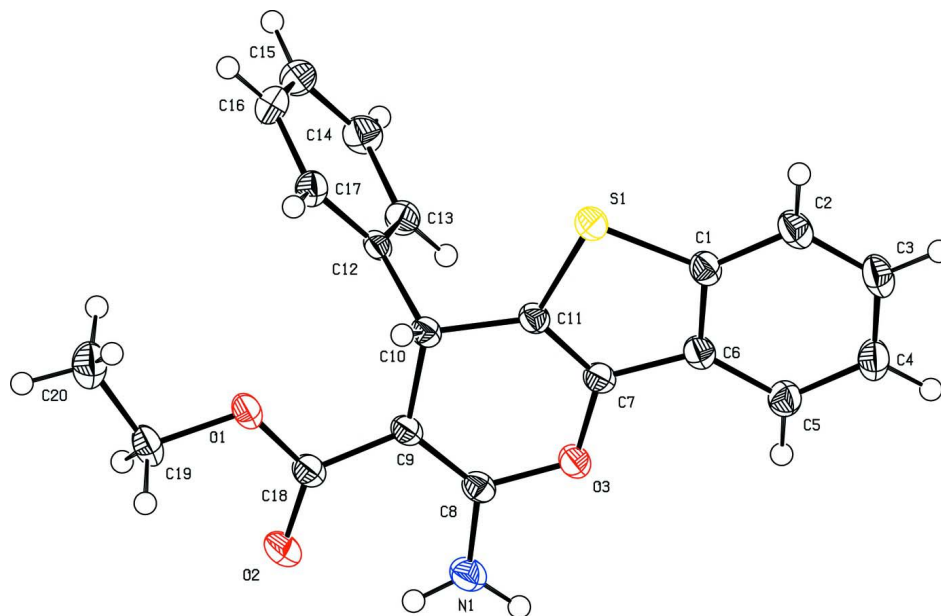
In the title compound, C₂₀H₁₇NO₃S (Fig. 1), the phenyl and ester groups make dihedral angles of 77.67 (6)° and 8.52 (6)°, respectively, with the benzothienopyran ring system. In the crystal, two molecules are linked about a center of inversion by pairs of N—H⋯O hydrogen bonds, generating a dimer (Fig. 2). Intermolecular C—H⋯N hydrogen bonds and C—H⋯ π interactions (between C15—H15 bond of the phenyl group and the centroid of the thiophene ring with symmetry code: *x*+1, *y*, *z*) are also observed (Table 1).

S2. Experimental

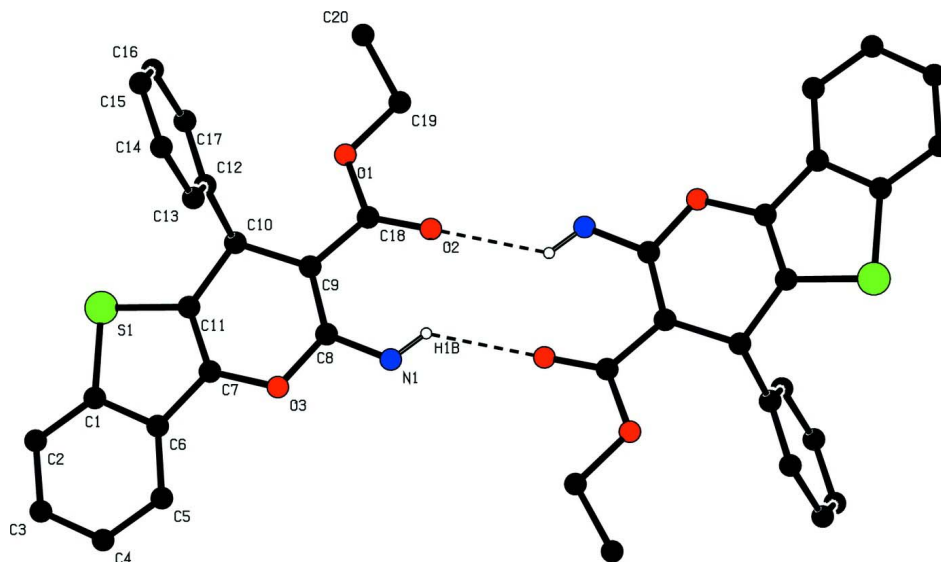
In a 100 ml flask equipped with a condenser, was dissolved 4 mmol of (*Z*)-2-benzylidenebenzo[*b*]thiophen-3(2*H*)-one and 5 mmol of ethyl cyanoacetate in 30 ml of ethanol. Then, 1ml of piperidine was added, and the reaction mixture was refluxed for 6 h. Thin layer chromatography revealed the formation of a single product. The organic phase was evaporated under reduced pressure. The resulting residue was recrystallized from ethanol.

S3. Refinement

All H atoms bound to C atoms were treated as riding to their parent atoms [C—H distances are 0.93 Å for aromatic CH groups, 0.97 Å for methylene CH₂ groups, 0.96 Å for the CH₃ methyl group, and 0.98 Å for the CH methine group]. Isotropic displacement parameters are calculated as $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C20})$ for the methyl group and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{parent C})$ for other H atoms. The amine H atoms H1A and H1B were found in a difference map, and refined with N—H bond lengths restrained to 0.88 (2) Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{N1})$.

**Figure 1**

Molecular view of the title compound showing displacement ellipsoids at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

**Figure 2**

Partial view of the crystal packing, showing the N—H...O bonded dimers (symmetry code: $-x, -y+1, -z$). H atoms not involved in hydrogen bonds have been omitted for clarity.

Ethyl 2-amino-4-phenyl-4*H*-1-benzothieno[3,2-*b*]pyran-3-carboxylate

Crystal data

$C_{20}H_{17}NO_3S$

$M_r = 351.41$

Monoclinic, $P2_1/n$

Hall symbol: $-P 2_1n$

$a = 8.6612 (3) \text{ \AA}$

$b = 5.9156 (2) \text{ \AA}$

$c = 32.3008 (10) \text{ \AA}$
 $\beta = 94.962 (2)^\circ$
 $V = 1648.77 (9) \text{ \AA}^3$
 $Z = 4$
 $F(000) = 736$
 $D_x = 1.416 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 232 reflections

$\theta = 2.6\text{--}25.3^\circ$
 $\mu = 0.22 \text{ mm}^{-1}$
 $T = 296 \text{ K}$
 Prism, colourless
 $0.25 \times 0.14 \times 0.12 \text{ mm}$

Data collection

Bruker APEXII CCD detector
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω and φ scans
 21683 measured reflections
 3608 independent reflections

3189 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 27.0^\circ$, $\theta_{\text{min}} = 2.4^\circ$
 $h = -11 \rightarrow 11$
 $k = -7 \rightarrow 7$
 $l = -41 \rightarrow 37$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.086$
 $S = 1.04$
 3608 reflections
 233 parameters
 2 restraints
 0 constraints
 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

$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.7884P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.18188 (4)	1.17172 (6)	0.191397 (10)	0.02581 (10)
O3	0.03012 (11)	0.62652 (16)	0.13342 (3)	0.0244 (2)
C9	0.15146 (15)	0.8299 (2)	0.08005 (4)	0.0209 (3)
C7	0.07313 (15)	0.8007 (2)	0.16060 (4)	0.0209 (3)
C12	0.39539 (14)	1.0315 (2)	0.11368 (4)	0.0191 (3)
C10	0.21849 (14)	1.0162 (2)	0.10886 (4)	0.0193 (3)
H10	0.1785	1.1610	0.0978	0.023*
C11	0.15652 (15)	0.9814 (2)	0.15042 (4)	0.0206 (3)
C6	0.02270 (15)	0.8029 (2)	0.20170 (4)	0.0219 (3)
C18	0.16810 (15)	0.8490 (2)	0.03571 (4)	0.0233 (3)
C8	0.06481 (15)	0.6545 (2)	0.09321 (4)	0.0212 (3)
C1	0.07339 (15)	1.0023 (2)	0.22215 (4)	0.0233 (3)
C2	0.03563 (16)	1.0502 (3)	0.26251 (4)	0.0280 (3)
H2	0.0692	1.1827	0.2759	0.034*
C5	-0.06701 (16)	0.6470 (3)	0.22184 (4)	0.0263 (3)
H5	-0.1011	0.5140	0.2087	0.032*
C4	-0.10381 (16)	0.6953 (3)	0.26180 (4)	0.0300 (3)
H4	-0.1633	0.5936	0.2756	0.036*
C13	0.48520 (16)	0.8567 (2)	0.13167 (4)	0.0246 (3)

H13	0.4379	0.7236	0.1392	0.030*
C17	0.46835 (16)	1.2279 (2)	0.10227 (4)	0.0240 (3)
H17	0.4097	1.3453	0.0899	0.029*
C19	0.26683 (17)	1.0704 (3)	-0.01709 (4)	0.0287 (3)
H19A	0.1676	1.0940	-0.0328	0.034*
H19B	0.3159	0.9389	-0.0282	0.034*
C3	-0.05272 (17)	0.8949 (3)	0.28169 (4)	0.0303 (3)
H3	-0.0790	0.9234	0.3085	0.036*
C16	0.62864 (17)	1.2511 (3)	0.10919 (5)	0.0294 (3)
H16	0.6764	1.3835	0.1015	0.035*
C14	0.64516 (16)	0.8792 (3)	0.13841 (4)	0.0292 (3)
H14	0.7043	0.7608	0.1503	0.035*
C15	0.71678 (16)	1.0774 (3)	0.12754 (4)	0.0305 (3)
H15	0.8236	1.0935	0.1326	0.037*
C20	0.36800 (19)	1.2749 (3)	-0.01999 (5)	0.0361 (4)
H20A	0.3148	1.4059	-0.0110	0.054*
H20B	0.3914	1.2954	-0.0483	0.054*
H20C	0.4625	1.2542	-0.0026	0.054*
O1	0.24544 (11)	1.03714 (17)	0.02657 (3)	0.0257 (2)
O2	0.11868 (12)	0.71560 (19)	0.00872 (3)	0.0319 (2)
N1	0.00146 (15)	0.4847 (2)	0.06999 (4)	0.0279 (3)
H1A	-0.062 (2)	0.392 (3)	0.0809 (5)	0.034*
H1B	0.009 (2)	0.484 (3)	0.0443 (6)	0.034*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02830 (19)	0.02802 (19)	0.02170 (17)	-0.00438 (14)	0.00562 (13)	-0.00647 (14)
O3	0.0311 (5)	0.0234 (5)	0.0187 (5)	-0.0041 (4)	0.0023 (4)	-0.0009 (4)
C9	0.0206 (6)	0.0245 (7)	0.0173 (6)	0.0016 (5)	-0.0005 (5)	-0.0016 (5)
C7	0.0192 (6)	0.0240 (7)	0.0191 (6)	0.0016 (5)	-0.0001 (5)	-0.0022 (5)
C12	0.0204 (6)	0.0240 (6)	0.0130 (5)	0.0008 (5)	0.0021 (5)	-0.0034 (5)
C10	0.0193 (6)	0.0209 (6)	0.0176 (6)	0.0024 (5)	0.0005 (5)	-0.0004 (5)
C11	0.0187 (6)	0.0243 (7)	0.0187 (6)	0.0019 (5)	0.0009 (5)	-0.0026 (5)
C6	0.0179 (6)	0.0284 (7)	0.0194 (6)	0.0054 (5)	0.0003 (5)	0.0005 (5)
C18	0.0218 (6)	0.0272 (7)	0.0206 (6)	0.0023 (5)	0.0000 (5)	-0.0018 (5)
C8	0.0211 (6)	0.0233 (7)	0.0185 (6)	0.0040 (5)	-0.0016 (5)	-0.0009 (5)
C1	0.0192 (6)	0.0297 (7)	0.0210 (6)	0.0042 (5)	0.0015 (5)	0.0004 (6)
C2	0.0274 (7)	0.0355 (8)	0.0209 (6)	0.0068 (6)	0.0016 (5)	-0.0035 (6)
C5	0.0233 (7)	0.0315 (7)	0.0241 (7)	0.0005 (6)	0.0011 (5)	0.0038 (6)
C4	0.0240 (7)	0.0422 (9)	0.0243 (7)	0.0034 (6)	0.0043 (5)	0.0094 (6)
C13	0.0254 (7)	0.0256 (7)	0.0227 (6)	0.0008 (5)	0.0007 (5)	0.0017 (6)
C17	0.0252 (7)	0.0249 (7)	0.0222 (6)	0.0017 (5)	0.0034 (5)	0.0021 (6)
C19	0.0335 (8)	0.0369 (8)	0.0161 (6)	0.0048 (6)	0.0034 (5)	0.0020 (6)
C3	0.0263 (7)	0.0460 (9)	0.0191 (6)	0.0104 (6)	0.0047 (5)	0.0023 (6)
C16	0.0266 (7)	0.0333 (8)	0.0292 (7)	-0.0055 (6)	0.0073 (6)	0.0016 (6)
C14	0.0246 (7)	0.0341 (8)	0.0282 (7)	0.0072 (6)	-0.0015 (6)	0.0021 (6)
C15	0.0192 (7)	0.0442 (9)	0.0283 (7)	-0.0003 (6)	0.0026 (5)	-0.0021 (7)

C20	0.0381 (9)	0.0423 (9)	0.0289 (8)	0.0019 (7)	0.0082 (6)	0.0084 (7)
O1	0.0322 (5)	0.0294 (5)	0.0157 (4)	-0.0024 (4)	0.0027 (4)	0.0003 (4)
O2	0.0390 (6)	0.0359 (6)	0.0206 (5)	-0.0061 (5)	0.0010 (4)	-0.0076 (4)
N1	0.0353 (7)	0.0262 (6)	0.0219 (6)	-0.0057 (5)	0.0001 (5)	-0.0029 (5)

Geometric parameters (Å, °)

S1—C11	1.7371 (13)	C5—H5	0.9300
S1—C1	1.7422 (14)	C4—C3	1.398 (2)
O3—C8	1.3681 (16)	C4—H4	0.9300
O3—C7	1.3839 (16)	C13—C14	1.390 (2)
C9—C8	1.3694 (19)	C13—H13	0.9300
C9—C18	1.4561 (18)	C17—C16	1.394 (2)
C9—C10	1.5247 (18)	C17—H17	0.9300
C7—C11	1.3465 (19)	C19—O1	1.4516 (15)
C7—C6	1.4330 (18)	C19—C20	1.501 (2)
C12—C17	1.3879 (19)	C19—H19A	0.9700
C12—C13	1.3905 (19)	C19—H19B	0.9700
C12—C10	1.5293 (17)	C3—H3	0.9300
C10—C11	1.5022 (17)	C16—C15	1.383 (2)
C10—H10	0.9800	C16—H16	0.9300
C6—C5	1.402 (2)	C14—C15	1.386 (2)
C6—C1	1.404 (2)	C14—H14	0.9300
C18—O2	1.2253 (17)	C15—H15	0.9300
C18—O1	1.3448 (17)	C20—H20A	0.9600
C8—N1	1.3421 (18)	C20—H20B	0.9600
C1—C2	1.4000 (18)	C20—H20C	0.9600
C2—C3	1.377 (2)	N1—H1A	0.871 (19)
C2—H2	0.9300	N1—H1B	0.838 (18)
C5—C4	1.386 (2)		
C11—S1—C1	91.31 (7)	C5—C4—C3	120.89 (14)
C8—O3—C7	116.29 (10)	C5—C4—H4	119.6
C8—C9—C18	117.89 (12)	C3—C4—H4	119.6
C8—C9—C10	123.22 (11)	C14—C13—C12	120.55 (13)
C18—C9—C10	118.65 (12)	C14—C13—H13	119.7
C11—C7—O3	123.83 (12)	C12—C13—H13	119.7
C11—C7—C6	115.61 (12)	C12—C17—C16	120.65 (13)
O3—C7—C6	120.49 (12)	C12—C17—H17	119.7
C17—C12—C13	118.85 (12)	C16—C17—H17	119.7
C17—C12—C10	119.85 (12)	O1—C19—C20	107.10 (12)
C13—C12—C10	121.19 (12)	O1—C19—H19A	110.3
C11—C10—C9	107.45 (11)	C20—C19—H19A	110.3
C11—C10—C12	110.46 (10)	O1—C19—H19B	110.3
C9—C10—C12	115.47 (10)	C20—C19—H19B	110.3
C11—C10—H10	107.7	H19A—C19—H19B	108.5
C9—C10—H10	107.7	C2—C3—C4	121.53 (13)
C12—C10—H10	107.7	C2—C3—H3	119.2

C7—C11—C10	124.58 (12)	C4—C3—H3	119.2
C7—C11—S1	111.31 (10)	C15—C16—C17	120.08 (14)
C10—C11—S1	124.10 (10)	C15—C16—H16	120.0
C5—C6—C1	119.86 (12)	C17—C16—H16	120.0
C5—C6—C7	130.52 (13)	C15—C14—C13	120.20 (13)
C1—C6—C7	109.59 (12)	C15—C14—H14	119.9
O2—C18—O1	121.79 (12)	C13—C14—H14	119.9
O2—C18—C9	126.25 (13)	C16—C15—C14	119.65 (13)
O1—C18—C9	111.95 (11)	C16—C15—H15	120.2
N1—C8—O3	109.09 (12)	C14—C15—H15	120.2
N1—C8—C9	127.01 (13)	C19—C20—H20A	109.5
O3—C8—C9	123.90 (12)	C19—C20—H20B	109.5
C2—C1—C6	121.28 (13)	H20A—C20—H20B	109.5
C2—C1—S1	126.56 (12)	C19—C20—H20C	109.5
C6—C1—S1	112.16 (10)	H20A—C20—H20C	109.5
C3—C2—C1	117.90 (14)	H20B—C20—H20C	109.5
C3—C2—H2	121.1	C18—O1—C19	115.69 (11)
C1—C2—H2	121.1	C8—N1—H1A	119.0 (11)
C4—C5—C6	118.54 (14)	C8—N1—H1B	119.6 (13)
C4—C5—H5	120.7	H1A—N1—H1B	120.2 (17)
C6—C5—H5	120.7		

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the thiophene ring.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1B...O2 ⁱ	0.838 (19)	2.285 (19)	2.9143 (16)	132.1 (15)
C10—H10...N1 ⁱⁱ	0.98	2.57	3.5189 (17)	164
C15—H15...Cg1 ⁱⁱⁱ	0.93	2.95	3.7493 (15)	145

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