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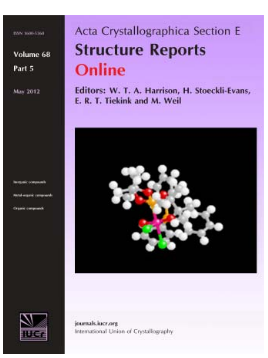

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(*E*)-3-(4-Bromo-5-methylthiophen-2-yl)-acrylonitrile

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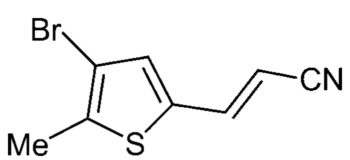
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.008 Å; R factor = 0.048; wR factor = 0.120; data-to-parameter ratio = 18.7.

In the title structure, C_8H_6BrNS, the molecules are planar with the exception of the methyl H atoms. In the crystal, molecules are linked by intermolecular C—H···N interactions to form ribbons parallel to the *b* axis. Groups of ribbons are arranged in a herringbone pattern to form a layered structure parallel to the *ab* plane.

Related literature

For related structures and their applications, see: Perner *et al.* (2003); Kose (2004); Chandra *et al.* (2006); Zhao *et al.* (2009); Pu *et al.* (2010); Dinçalp *et al.* (2011).



Experimental

Crystal data

C_8H_6BrNS
M_r = 228.11
Orthorhombic, $P2_12_12_1$
a = 6.1347 (5) Å
b = 7.1124 (3) Å
c = 19.8245 (13) Å
V = 864.99 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.92 mm^{-1}
T = 150 K
0.40 × 0.30 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: empirical (using intensity measurements) (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.243, T_{max} = 0.639
3294 measured reflections
1910 independent reflections
1769 reflections with $I > 2\sigma(I)$
R_{int} = 0.060

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.120
S = 1.05
1910 reflections
102 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.74 e Å^{-3}
$\Delta\rho_{min}$ = −1.12 e Å^{-3}
Absolute structure: Flack (1983), 699 Friedel pairs
Absolute structure parameter: 0.03 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···N1^{i}	0.93	2.59	3.501 (8)	166

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

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *CHEMDRAW Ultra* (Cambridge Soft, 2001).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG5330).

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supplementary materials

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(*E*)-3-(4-Bromo-5-methylthiophen-2-yl)acrylonitrile

Gamal A. El-Hiti, Keith Smith, Asim A. Balakit, Ali Masmali and Benson M. Kariuki

1. Comment

During the research focused on new synthetic routes towards novel substituted thiophene derivatives, we have synthesized the title compound (I), which was isolated in high yield. Thiophene derivatives are interesting compounds (Zhao *et al.*, 2009). They can be used in a wide range of applications such as enzyme inhibitors (Perner *et al.*, 2003), photochromic materials (Kose, 2004; Pu *et al.*, 2010), bioprobes (Chandra *et al.*, 2006) and dyes (Dinçalp *et al.*, 2011).

In the structure, the molecules of (*E*)-3-(4-bromo-5-methylthiophen-2-yl)-acrylonitrile (I) are planar, except for H atoms of the methyl group (Fig. 1). The molecules are linked by C—H···N interactions (Table 1) to form corrugated ribbons. The ribbons run parallel to the *b* axis and, within a ribbon, the orientation of consecutive molecules alternates to the left and right (Fig. 2). Groups of ribbons are arranged in a herringbone pattern to form a layered structure with layers parallel to the *ab* plane (Fig. 3).

2. Experimental

Synthesis of *E*-3-(4-bromo-5-methylthiophen-2-yl)acrylonitrile (I)

Diethyl (cyanomethyl)phosphonate (0.94 g, 5.3 mmol) was added to sodium hydride (6.25 mmol) suspended in dry THF (50 ml) under inert atmosphere. The mixture was stirred for 1 h, 3-bromo-2-methylthiophene-5-carboxaldehyde (1.00 g, 4.90 mmol) was added and stirring was continued overnight. Saturated aqueous ammonium chloride solution (25 ml) was added and the mixture was extracted with diethyl ether (4 × 50 ml). The organic phase was washed with saturated aqueous sodium hydrogen carbonate solution (50 ml) and brine (25 ml) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the crude product was separated by column chromatography (silica gel, Et_2O:hexane in 1:1 by volume) to give a mixture of *E*- and *Z*-isomers of 3-(4-bromo-5-methylthiophen-2-yl)acrylonitrile in 4:1 ratio. m.p. 80–81°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, p.p.m.): 7.23 (d, J = 16.3 Hz, 0.8H), 7.20 (d, J = 11.7 Hz, 0.2H), 6.98 (s, 1H), 5.46 (d, J = 16.3 Hz, 0.8H), 5.15 (d, J = 11.7 Hz, 0.2H), 2.37 (s, 0.6H), 2.35 (s, 2.4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, p.p.m.): 141.6 (*d*), 140.0 (*d*), 138.9 (*s*), 135.2 (*s*), 134.8 (*d*), 133.5 (*d*), 117.8 (*s*), 110.9 (*s*), 94.5 (*d*), 91.2 (*d*), 15.4 (*q*). EI–MS (m/*z*, %): 229 ([M ^{81}Br]$^+$, 80), 227 ([M ^{79}Br]$^+$, 78), 148 (100), 121 (10). HRMS (EI): Calculated for C_8H_6BrNS [M ^{79}Br]$^+$ 226.9404; found: 226.9402. FT–IR (ν_{max}, cm^{-1}): 2211. Recrystallization from diethyl ether gave colorless crystals of the *E*-isomer (I).

3. Refinement

H atoms were positioned geometrically and refined using a riding model. For sp^2 H atoms, U_{iso}(H) is constrained to 1.2 times the U_{eq} for the atoms they are bonded to and the C—H distance is 0.93 Å. For the methyl group, U_{iso}(H) is 1.5 times the U_{eq} for C atom they are bonded to and the C—H distance is 0.96 Å, with free rotation about the C—C bond.

Computing details

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *CHEMDRAW* Ultra (Cambridge Soft, 2001).

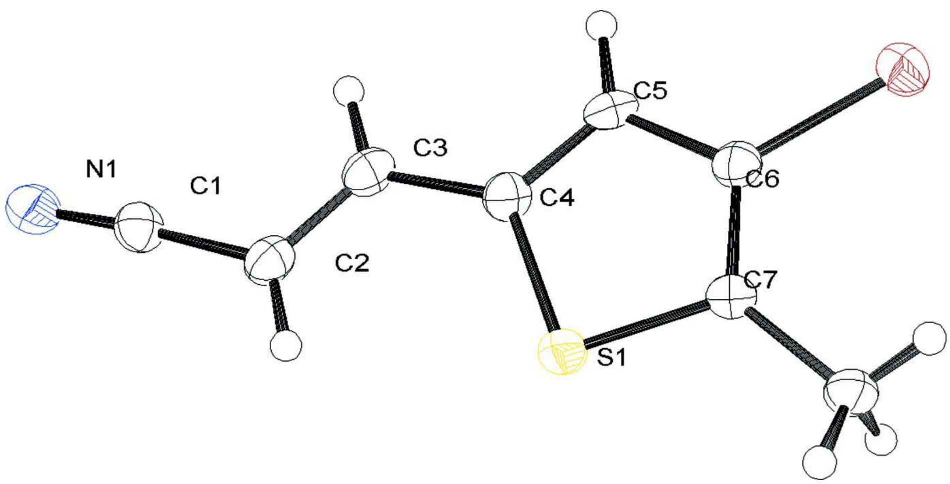

Figure 1

A molecule of I showing atom labels and 50% probability displacement ellipsoids for non-H atoms.

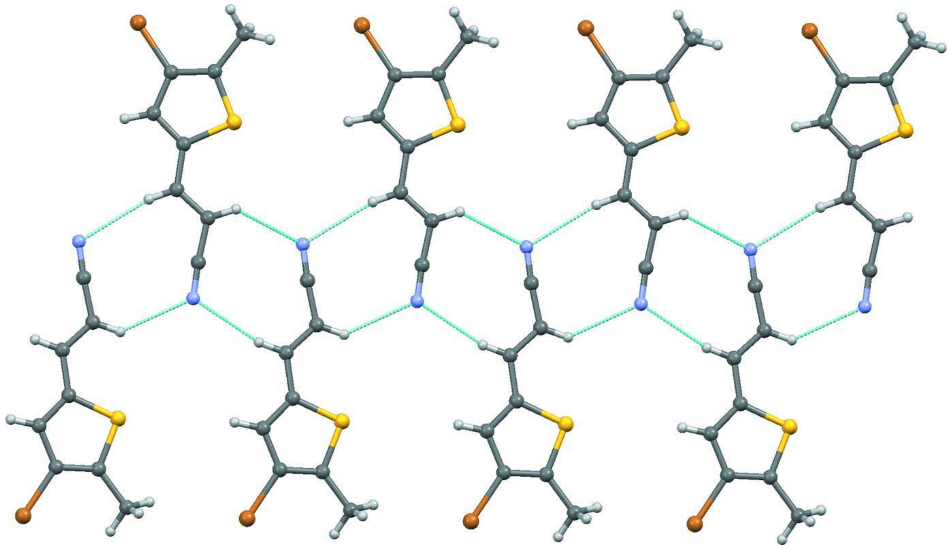

Figure 2

A segment of the crystal structure showing C—H···N interactions as dashed lines.

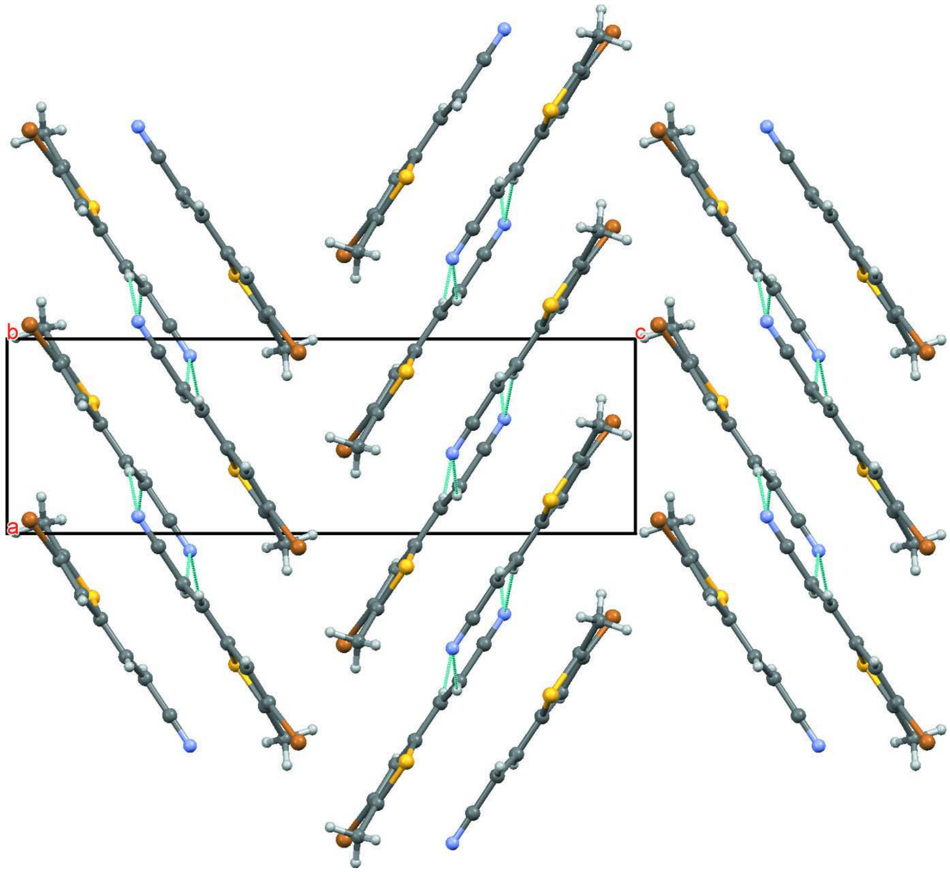

Figure 3

A segment of the crystal structure of I showing the herringbone arrangement to form layers of ribbons.

(*E*)-3-(4-Bromo-5-methylthiophen-2-yl)acrylonitrile

Crystal data

C_8H_6BrNS
M_r = 228.11
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 6.1347 (5) Å
b = 7.1124 (3) Å
c = 19.8245 (13) Å
V = 864.99 (10) Å^3
Z = 4
F(000) = 448
D_x = 1.752 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1769 reflections
θ = 3.0–28.4°
μ = 4.92 mm^{-1}
T = 150 K
Plate, yellow
0.40 × 0.30 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
CCD scans
Absorption correction: empirical (using intensity measurements) (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.243, T_{max} = 0.639
3294 measured reflections
1910 independent reflections
1769 reflections with $I > 2\sigma(I)$
R_{int} = 0.060
θ_{max} = 27.4°, θ_{min} = 3.0°
h = −4→7
k = −9→7
l = −25→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.120$
$S = 1.05$
1910 reflections
102 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 2.3854P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.74$ e Å^{-3}
$\Delta\rho_{min} = -1.12$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.030 (3)
Absolute structure: Flack (1983), 699 Friedel pairs
Absolute structure parameter: 0.03 (2)

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}
C1	−0.4336 (10)	−0.1420 (8)	0.7590 (3)	0.0265 (11)
C2	−0.2429 (10)	−0.1841 (9)	0.7200 (3)	0.0264 (12)
H2	−0.1959	−0.3079	0.7159	0.032*
C3	−0.1322 (9)	−0.0462 (8)	0.6895 (3)	0.0258 (12)
H3	−0.1824	0.0764	0.6946	0.031*
C4	0.0617 (10)	−0.0763 (7)	0.6489 (3)	0.0235 (11)
C5	0.1860 (10)	0.0569 (8)	0.6186 (3)	0.0222 (11)
H5	0.1553	0.1849	0.6203	0.027*
C6	0.3668 (10)	−0.0199 (8)	0.5843 (3)	0.0241 (12)
C7	0.3838 (8)	−0.2120 (7)	0.5887 (2)	0.0191 (11)
C8	0.5528 (11)	−0.3400 (7)	0.5583 (3)	0.0264 (12)
H8A	0.5059	−0.3791	0.5142	0.040*
H8B	0.5713	−0.4485	0.5865	0.040*
H8C	0.6888	−0.2741	0.5546	0.040*
N1	−0.5883 (9)	−0.1203 (8)	0.7912 (3)	0.0331 (11)
S1	0.1701 (3)	−0.2987 (2)	0.63524 (7)	0.0246 (3)
Br1	0.57000 (10)	0.12692 (8)	0.53635 (3)	0.0319 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.022 (3)	0.028 (3)	0.030 (3)	−0.001 (3)	0.000 (2)	0.000 (2)
C2	0.024 (3)	0.027 (3)	0.029 (3)	0.003 (2)	0.001 (2)	−0.005 (2)

C3	0.023 (3)	0.025 (3)	0.029 (3)	0.006 (2)	−0.002 (2)	−0.003 (2)
C4	0.016 (2)	0.025 (3)	0.030 (3)	0.003 (2)	−0.002 (2)	−0.001 (2)
C5	0.023 (3)	0.018 (2)	0.026 (3)	0.004 (2)	−0.006 (2)	−0.006 (2)
C6	0.025 (3)	0.024 (3)	0.023 (3)	−0.001 (2)	−0.001 (2)	−0.004 (2)
C7	0.021 (3)	0.019 (2)	0.017 (2)	0.002 (2)	−0.0057 (19)	0.0017 (19)
C8	0.032 (3)	0.019 (3)	0.028 (3)	0.002 (2)	0.002 (2)	0.003 (2)
N1	0.031 (3)	0.031 (2)	0.038 (3)	−0.008 (3)	0.002 (2)	−0.004 (2)
S1	0.0240 (7)	0.0207 (6)	0.0291 (7)	0.0007 (6)	0.0021 (6)	−0.0004 (5)
Br1	0.0332 (3)	0.0259 (3)	0.0368 (3)	−0.0021 (3)	0.0065 (3)	0.0040 (2)

Geometric parameters (Å, º)

C1—N1	1.154 (8)	C5—H5	0.9300
C1—C2	1.434 (8)	C6—C7	1.373 (7)
C2—C3	1.338 (8)	C6—Br1	1.884 (6)
C2—H2	0.9300	C7—C8	1.506 (8)
C3—C4	1.452 (8)	C7—S1	1.717 (5)
C3—H3	0.9300	C8—H8A	0.9600
C4—C5	1.356 (8)	C8—H8B	0.9600
C4—S1	1.737 (5)	C8—H8C	0.9600
C5—C6	1.412 (8)		
N1—C1—C2	175.6 (7)	C7—C6—C5	114.5 (5)
C3—C2—C1	120.3 (5)	C7—C6—Br1	122.3 (4)
C3—C2—H2	119.8	C5—C6—Br1	123.3 (4)
C1—C2—H2	119.8	C6—C7—C8	128.9 (5)
C2—C3—C4	123.9 (5)	C6—C7—S1	109.5 (4)
C2—C3—H3	118.0	C8—C7—S1	121.6 (4)
C4—C3—H3	118.0	C7—C8—H8A	109.5
C5—C4—C3	127.1 (5)	C7—C8—H8B	109.5
C5—C4—S1	110.6 (4)	H8A—C8—H8B	109.5
C3—C4—S1	122.3 (4)	C7—C8—H8C	109.5
C4—C5—C6	112.6 (5)	H8A—C8—H8C	109.5
C4—C5—H5	123.7	H8B—C8—H8C	109.5
C6—C5—H5	123.7	C7—S1—C4	92.8 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···N1^{i}	0.93	2.59	3.501 (8)	166

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