Ethyl 4-cyano-5-iodo-3-methylthiophene-2-carboxylate

Jan Moncol,[a]* Zita Puterová[b] and Daniel Végh[b]

[a]Institute of Inorganic Chemistry, Technology and Materials, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovakia, and [b]Institute of Organic Chemistry, Catalysis and Petrochemistry, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovakia
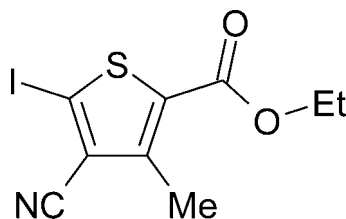Correspondence e-mail: jan.moncol@stuba.sk

The title compound, $C_9H_8INO_2S$, was synthesized by starting from ethyl 5-amino-4-cyano-3-methylthiophene-2-carboxylate *via* Sandmeyer-type deamination, replacing the NH_2 group by iodine. In the crystal structure, molecules form a two-membered cyclamer held together by $CN\cdots I$ intermolecular Lewis acid–base interactions. The $N\cdots I$ distance, and $C-I\cdots N$ and $N\cdots I-C$ angles are 3.142 (3) Å, 166.9 (1)° and 123.1 (1)°, respectively.

Related literature

For related literature, see: Apinitis *et al.* (1984); Bailey *et al.* (2000); Bond *et al.* (2001); Britton (2001, 2004); Britton & Gleason (2002); Desiraju & Harlow (1989); Metrangolo *et al.* (2004); Nyburg & Faerman (1985); Ojala *et al.* (1999).

Experimental

Crystal data

$C_9H_8INO_2S$	γ = 86.166 (2)°
M_r = 321.12	V = 558.23 (3) Å³
Triclinic, $P\overline{1}$	Z = 2
a = 4.3132 (1) Å	Mo $K\alpha$ radiation
b = 9.4355 (3) Å	μ = 3.03 mm^{-1}
c = 13.8210 (4) Å	T = 298 (2) K
α = 87.736 (2)°	$0.73 \times 0.10 \times 0.06$ mm
β = 84.396 (2)°	

Data collection

Oxford Diffraction Gemini R CCD diffractometer	16856 measured reflections
Absorption correction: analytical (Clark & Reid, 1995)	2663 independent reflections
T_{min} = 0.383, T_{max} = 0.872	1947 reflections with $I > 2\sigma(I)$
	R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026	129 parameters
$wR(F^2)$ = 0.067	H-atom parameters constrained
S = 1.02	$\Delta\rho_{max}$ = 0.95 e Å^{-3}
2663 reflections	$\Delta\rho_{min}$ = −0.47 e Å^{-3}

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C9—H9C⋯O2	0.96	2.55	3.031 (4)	111

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2315).

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supplementary materials

Ethyl 4-cyano-5-iodo-3-methylthiophene-2-carboxylate

J. Moncol, Z. Puterová and **D. Végh**

Comment

The family of well defined oligothiophene derivatives is important for polymer research, electronic semiconducting materials, non-linear optical materials and highly ordered molecular assemblies. Thiophene based oligomers are among the most investigated systems for technological applications, due to their chemical stability and wide spread possibility of functionalization. Moreover, they are relative to some other conjugated systems and represent structures with high labeled molecular architecture. Etyl 5-iodo-4-cyano-3-methylthiophene-2-carboxylate represents an important building block in desing of oligothiophene structure, in terms of its well defined molecular structure. We report herein the crystal structure of the title compound, (I).

In the molecule of the title compound, (I), (Fig. 1), the bond lengths are in accordance with those observed in ethyl 5-amino-4-cyano-3-methylthiophene-2-carboxylate (refcode: DACLIC; Apinitis *et al.*, 1984). A weak intramolecular C—H⋯O hydrogen bond (Table 1) is also comparable with the corresponding one in DACLIC.

A cyclamer is formed by the association of two monomers through weak intermolecular CN⋯I Lewis acid-base interactions (Fig. 2). The CN⋯I distances are in accordance with the expected values from non-spherical radii of Nyburg & Faerman (1985). The angles at the N atoms are closer to trigonal, but the angles at the I atoms are approximately linear. In (I), the N⋯I distance, C—I⋯N and N⋯I—C angles are 3.142 (3) Å, 166.9 (1)° and 123.1 (1)°, respectively. The significant CN⋯I interactions (in the range of 2.9–3.3 Å) are well known in more organic molecules containing iodo and cyano groups (Bond *et al.*, 2001; Britton, 2001, 2004; Desiraju & Harlow, 1989; Ojala *et al.*, 1999), and as well as in organic co-crystals, organic cyano- and iodo-compounds (Bailey *et al.*, 2000; Britton & Gleason, 2002; Metrangolo *et al.*, 2004).

Experimental

For the preparation of the title compound, (I), etyl 5-amino-4-cyano-3-methylthiophene-2-carboxylate (12.0 mmol, 2.5 g) was added to a solution of *p*-toluenesulphonic acid (36.0 mmol, 6.4 g) in acetonitrile (50 ml). The resulting solution was cooled to 283–288 K and added to a solution of $NaNO_2$ (1.6 g, 24 mmol) and KI (5.2 g, 30 mmol) in water (10 ml), gradually. The reaction mixture was stirred for 10 min, then allowed to come 293 K and stirred for 3 h. Then, H_2O (50 ml), $NaHCO_3$ (1 *M*, until pH = 9–10) and $Na_2S_2O_3$ (2 *M*, 6 ml) were added to the reaction mixture. The precipitated iodine was filtered and purified by flash flow column chromatography (i-hexane/ethylacetate, 5:1) (yield: 2.7 g, 73%, m.p. 395–398 K).

Refinement

H atoms were positioned geometrically, with C—H = 0.97 and 0.96 Å for methylene and methyl H, and constrained to ride on their parent atoms, with $U_{iso}(H) = x U_{eq}(C)$, where $x = 1.2$ for methylene H, and $x = 1.5$ for methyl H atoms.
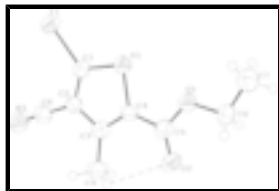
supplementary materials

Figures

Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
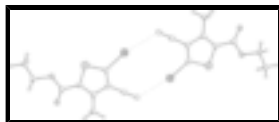

Fig. 2. Two-membered cyclamers of (I), through CN···I intermolecular interactions.

Ethyl 4-cyano-5-iodo-3-methylthiophene-2-carboxylate

Crystal data

$C_9H_8INO_2S$	$Z = 2$
$M_r = 321.12$	$F_{000} = 308$
Triclinic, $P\bar{1}$	$D_x = 1.910$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71069$ Å
$a = 4.3132$ (1) Å	Cell parameters from 9412 reflections
$b = 9.4355$ (3) Å	$\theta = 3.6–29.5°$
$c = 13.8210$ (4) Å	$\mu = 3.03$ mm^{-1}
$\alpha = 87.736$ (2)°	$T = 298$ (2) K
$\beta = 84.396$ (2)°	Needle, colourless
$\gamma = 86.166$ (2)°	$0.73 \times 0.10 \times 0.06$ mm
$V = 558.23$ (3) Å^3	

Data collection

Oxford Diffraction Gemini R CCD diffractometer	2663 independent reflections
Radiation source: fine-focus sealed tube	1947 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.039$
Detector resolution: 10.4340 pixels mm^{-1}	$\theta_{max} = 28.0°$
$T = 298(2)$ K	$\theta_{min} = 3.6°$
ω and φ scans	$h = -5 \rightarrow 5$
Absorption correction: analytical (Clark & Reid, 1995)	$k = -12 \rightarrow 12$
$T_{min} = 0.383$, $T_{max} = 0.872$	$l = -18 \rightarrow 18$
16856 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.026$

H-atom parameters constrained

$wR(F^2) = 0.067$

$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$S = 1.02$

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

2663 reflections

$\Delta\rho_{max} = 0.95$ e Å^{-3}

129 parameters

$\Delta\rho_{min} = -0.47$ e Å^{-3}

Primary atom site location: structure-invariant direct methods

Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
I1	0.22760 (4)	−0.076548 (19)	0.127435 (14)	0.05116 (10)
S1	0.53223 (18)	0.09997 (8)	0.29133 (6)	0.04452 (18)
N1	0.0199 (8)	0.3059 (3)	−0.0005 (2)	0.0684 (8)
O1	0.7918 (5)	0.2529 (2)	0.43010 (15)	0.0511 (5)
O2	0.7225 (6)	0.4763 (2)	0.36908 (17)	0.0631 (6)
C1	0.3505 (6)	0.1064 (3)	0.1876 (2)	0.0417 (7)
C2	0.3038 (6)	0.2436 (3)	0.1528 (2)	0.0407 (6)
C3	0.4183 (7)	0.3469 (3)	0.2102 (2)	0.0425 (7)
C4	0.5503 (7)	0.2834 (3)	0.2882 (2)	0.0400 (6)
C5	0.6954 (7)	0.3497 (3)	0.3649 (2)	0.0438 (7)
C6	0.9331 (8)	0.3055 (4)	0.5121 (2)	0.0561 (8)
H6A	0.7802	0.3640	0.5515	0.067*
H6B	1.1052	0.3629	0.4889	0.067*
C7	1.0460 (11)	0.1831 (4)	0.5701 (3)	0.0777 (12)
H7A	0.8713	0.1360	0.6018	0.117*
H7B	1.1698	0.2147	0.6181	0.117*
H7C	1.1710	0.1182	0.5283	0.117*
C8	0.1475 (8)	0.2777 (3)	0.0666 (2)	0.0494 (8)
C9	0.3939 (9)	0.5037 (3)	0.1845 (3)	0.0615 (9)
H9A	0.2195	0.5483	0.2229	0.092*
H9B	0.3645	0.5175	0.1167	0.092*
H9C	0.5821	0.5452	0.1975	0.092*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.05619 (16)	0.04507 (14)	0.05412 (16)	−0.00672 (9)	−0.00908 (10)	−0.00998 (9)
S1	0.0518 (4)	0.0387 (4)	0.0444 (4)	−0.0020 (3)	−0.0121 (3)	−0.0014 (3)
N1	0.086 (2)	0.0612 (18)	0.0629 (19)	0.0001 (16)	−0.0329 (17)	−0.0107 (15)
O1	0.0613 (13)	0.0456 (12)	0.0504 (13)	−0.0053 (10)	−0.0236 (10)	−0.0031 (10)
O2	0.0886 (17)	0.0412 (12)	0.0651 (15)	−0.0122 (11)	−0.0278 (12)	−0.0065 (11)
C1	0.0403 (15)	0.0451 (16)	0.0405 (16)	−0.0021 (13)	−0.0063 (12)	−0.0069 (13)
C2	0.0416 (15)	0.0429 (16)	0.0380 (16)	−0.0045 (13)	−0.0059 (12)	0.0019 (13)
C3	0.0412 (15)	0.0398 (15)	0.0468 (17)	−0.0028 (13)	−0.0050 (13)	−0.0029 (13)
C4	0.0427 (16)	0.0338 (14)	0.0433 (16)	−0.0007 (12)	−0.0047 (13)	−0.0005 (12)
C5	0.0403 (16)	0.0478 (18)	0.0437 (17)	−0.0058 (14)	−0.0028 (13)	−0.0043 (14)
C6	0.068 (2)	0.057 (2)	0.0474 (18)	−0.0104 (17)	−0.0223 (16)	−0.0065 (15)
C7	0.109 (3)	0.069 (2)	0.061 (2)	−0.021 (2)	−0.031 (2)	0.0047 (19)
C8	0.0560 (19)	0.0422 (17)	0.0503 (19)	−0.0011 (15)	−0.0094 (16)	0.0001 (14)
C9	0.079 (2)	0.0405 (18)	0.068 (2)	−0.0041 (17)	−0.0247 (19)	0.0023 (16)

Geometric parameters (Å, °)

I1—C1	2.067 (3)	C3—C9	1.507 (4)
S1—C1	1.697 (3)	C4—C5	1.464 (4)
S1—C4	1.736 (3)	C6—C7	1.463 (5)
N1—C8	1.138 (4)	C6—H6A	0.9700
O1—C5	1.333 (4)	C6—H6B	0.9700
O1—C6	1.457 (4)	C7—H7A	0.9600
O2—C5	1.212 (4)	C7—H7B	0.9600
C1—C2	1.372 (4)	C7—H7C	0.9600
C2—C3	1.424 (4)	C9—H9A	0.9600
C2—C8	1.440 (4)	C9—H9B	0.9600
C3—C4	1.367 (4)	C9—H9C	0.9600
C1—S1—C4	91.75 (14)	O1—C6—H6A	110.1
C5—O1—C6	116.8 (2)	C7—C6—H6A	110.1
C2—C1—S1	111.3 (2)	O1—C6—H6B	110.1
C2—C1—I1	127.3 (2)	C7—C6—H6B	110.1
S1—C1—I1	121.34 (16)	H6A—C6—H6B	108.4
C1—C2—C3	114.0 (2)	C6—C7—H7A	109.5
C1—C2—C8	122.1 (3)	C6—C7—H7B	109.5
C3—C2—C8	123.9 (3)	H7A—C7—H7B	109.5
C4—C3—C2	110.7 (3)	C6—C7—H7C	109.5
C4—C3—C9	126.6 (3)	H7A—C7—H7C	109.5
C2—C3—C9	122.7 (3)	H7B—C7—H7C	109.5
C3—C4—C5	128.7 (3)	N1—C8—C2	178.8 (4)
C3—C4—S1	112.2 (2)	C3—C9—H9A	109.5
C5—C4—S1	119.1 (2)	C3—C9—H9B	109.5
O2—C5—O1	124.4 (3)	H9A—C9—H9B	109.5
O2—C5—C4	124.4 (3)	C3—C9—H9C	109.5

O1—C5—C4	111.2 (2)	H9A—C9—H9C	109.5
O1—C6—C7	108.2 (3)	H9B—C9—H9C	109.5
C4—S1—C1—C2	−0.5 (2)	C9—C3—C4—S1	−179.7 (3)
C4—S1—C1—I1	179.25 (17)	C1—S1—C4—C3	0.5 (2)
S1—C1—C2—C3	0.5 (3)	C1—S1—C4—C5	−179.8 (2)
I1—C1—C2—C3	−179.3 (2)	C6—O1—C5—O2	1.2 (4)
S1—C1—C2—C8	−178.6 (2)	C6—O1—C5—C4	−178.3 (3)
I1—C1—C2—C8	1.6 (4)	C3—C4—C5—O2	−1.0 (5)
C1—C2—C3—C4	−0.1 (4)	S1—C4—C5—O2	179.3 (3)
C8—C2—C3—C4	179.0 (3)	C3—C4—C5—O1	178.5 (3)
C1—C2—C3—C9	179.4 (3)	S1—C4—C5—O1	−1.1 (3)
C8—C2—C3—C9	−1.6 (5)	C5—O1—C6—C7	−175.3 (3)
C2—C3—C4—C5	180.0 (3)	C1—C2—C8—N1	116 (18)
C9—C3—C4—C5	0.5 (5)	C3—C2—C8—N1	−63 (18)
C2—C3—C4—S1	−0.3 (3)		

Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C9—H9C⋯O2	0.96	2.55	3.031 (4)	111

Fig. 1

Fig. 2