

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Methyl 4-(trifluoromethyl)-1H-pyrrole-3-carboxylate

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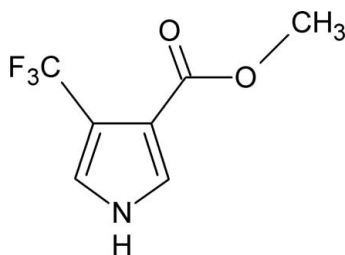
Received 9 September 2013; accepted 13 September 2013

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.065; wR factor = 0.180; data-to-parameter ratio = 8.7.

In the title compound, $\text{C}_7\text{H}_6\text{F}_3\text{NO}_2$, all the non-H atoms except for one of the F atoms lie on a crystallographic mirror plane. In the crystal, the molecules are linked into inversion dimers by pairs of $\text{C}-\text{H}\cdots\text{F}$ interactions, forming $R_2^2(10)$ loops. These dimers are connected into $\text{C}(6)$ chains along $[001]$ through $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds. Aromatic $\pi-\pi$ stacking interactions [centroid-centroid separation = $3.8416(10)$ Å] connect the molecules into a three-dimensional network.

Related literature

For background to the pharmacological activity of pyrrole derivatives, see: Toja *et al.* (1987); Muchowski *et al.* (1985); Dannhardt *et al.* (2000); Burnham *et al.* (1998); Krowicki *et al.* (1988).



Experimental

Crystal data

 $\text{C}_7\text{H}_6\text{F}_3\text{NO}_2$ $M_r = 193.13$

Monoclinic, $C2/m$
 $a = 16.643(2)$ Å
 $b = 7.1118(10)$ Å
 $c = 6.9618(11)$ Å
 $\beta = 98.903(7)^\circ$
 $V = 814.1(2)$ Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.16$ mm⁻¹
 $T = 293$ K
 $0.24 \times 0.22 \times 0.20$ mm

Data collection

Bruker APEXII CCD
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker, 2009)
 $T_{\min} = 0.963$, $T_{\max} = 0.969$

3752 measured reflections
 707 independent reflections
 645 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.076$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.180$
 $S = 1.09$
 707 reflections
 81 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.37$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N}-\text{H}\cdots\text{O1}^i$	0.83 (6)	2.03 (5)	2.810 (4)	156
$\text{C5}-\text{H5}\cdots\text{F1}^{ii}$	0.93	2.52	3.442 (4)	171

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT-Plus (Bruker, 2009); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: Mercury (Macrae *et al.*, 2008); software used to prepare material for publication: SHELXL97.

The authors acknowledge the IOE X-ray diffractometer Facility, University of Mysore, Mysore, for collecting the data.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB7136).

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supporting information

Acta Cryst. (2013). E69, o1566 [doi:10.1107/S160053681302549X]

Methyl 4-(trifluoromethyl)-1H-pyrrole-3-carboxylate

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S1. Comment

Pyrrole derivatives are given considerable attention due to their synthetic importance and their extensive use in drug discovery (Toja *et al.*, 1987) and pharmacological activity such as anti-inflammatory (Muchowski *et al.*, 1985), cytotoxicity (Dannhardt *et al.*, 2000), *in vitro* cytotoxic activity against solid tumour models (Burnham *et al.*, 1998), antitumour agents (Krowicki *et al.*, 1988] *etc.* As part of our studies in this area, the title compound was synthesized and its structure determined.

In the title compound, C₇H₆F₃NO₂, the C=O and O—C(methoxy) bonds are *syn* to each other (Fig 1). The molecules are linked into inversion dimers along *a* axis through C5—H5···F1 interactions, thus forming *R*₂²(10) loops (Fig 2). These dimers are further connected into C(6) chains through strong N—H···O1 hydrogen bonds along *c* axis (Fig 2). Further, π - π stacking interactions [centroid-centroid separation = 3.8416 (10) Å] connects the molecules into a three dimensional network (Fig 3).

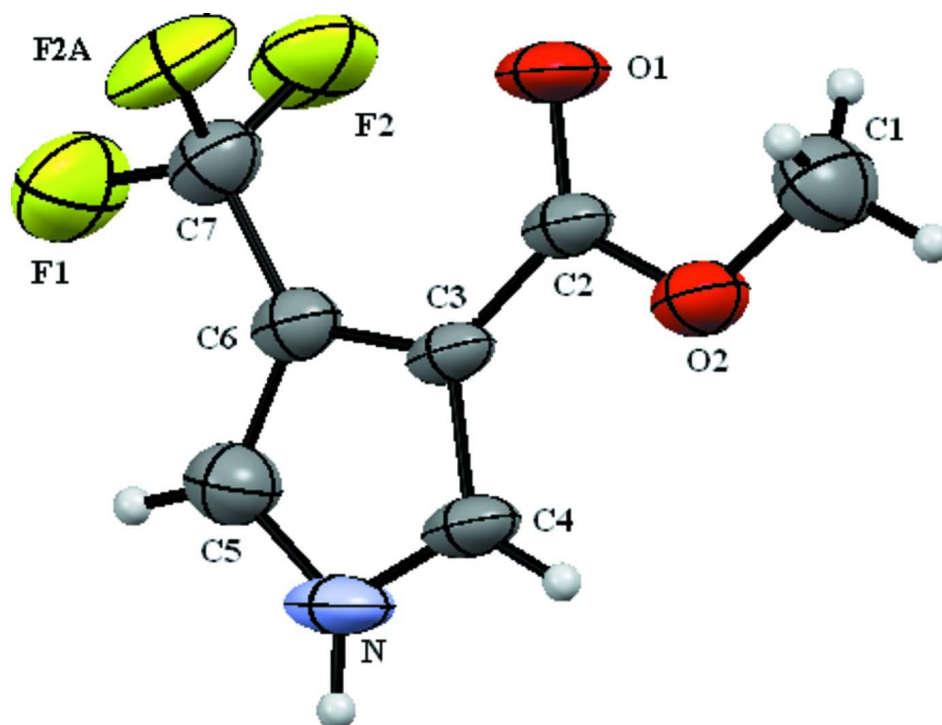
S2. Experimental

Sodium hydride (0.02 mol) and methyl 4,4,4-trifluorobut-2-enoate (0.01 mol) were taken in dry Tetrahydrofuran (THF). The reaction mixture was stirred for 15 min. Toluenesulfonylmethyl isocyanide (TosMIC, 0.01 mol) was added to the reaction mixture and the mixture was heated to 50°C for 2 h. Reaction was monitored by TLC. Ethyl acetate was added to the mixture. Sodium hydride was quenched by using saturated solution of ammonium chloride and the organic layer was separated, dried and concentrated. The crude compound was purified by column chromatography using petroleum ether / ethyl acetate (7:3) as eluent to give the title compound as a colorless solid.

Colourless prisms were obtained from slow evaporation of the solution of the compound in a mixture of petroleum ether/ethyl acetate (7:3).

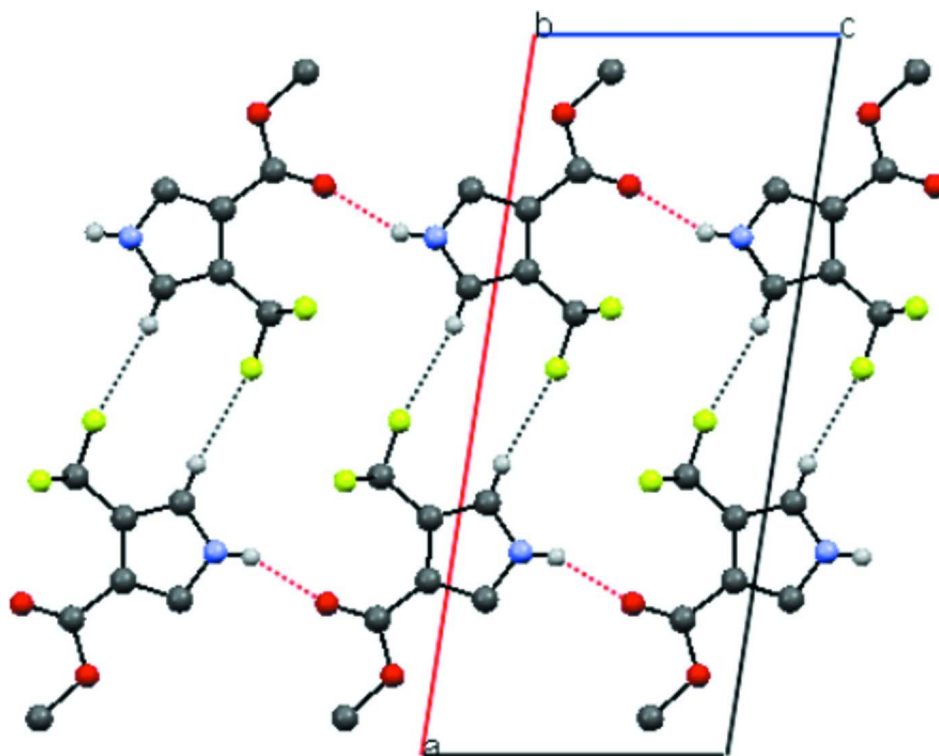
S3. Refinement

The H atom of the NH group was located in a difference map and later refined freely. The other H atoms were positioned with idealized geometry using a riding model with C—H = 0.93–0.96 Å. All H atoms were refined with isotropic displacement parameters (set to 1.2 times of the *U*_{eq} of the parent atom).

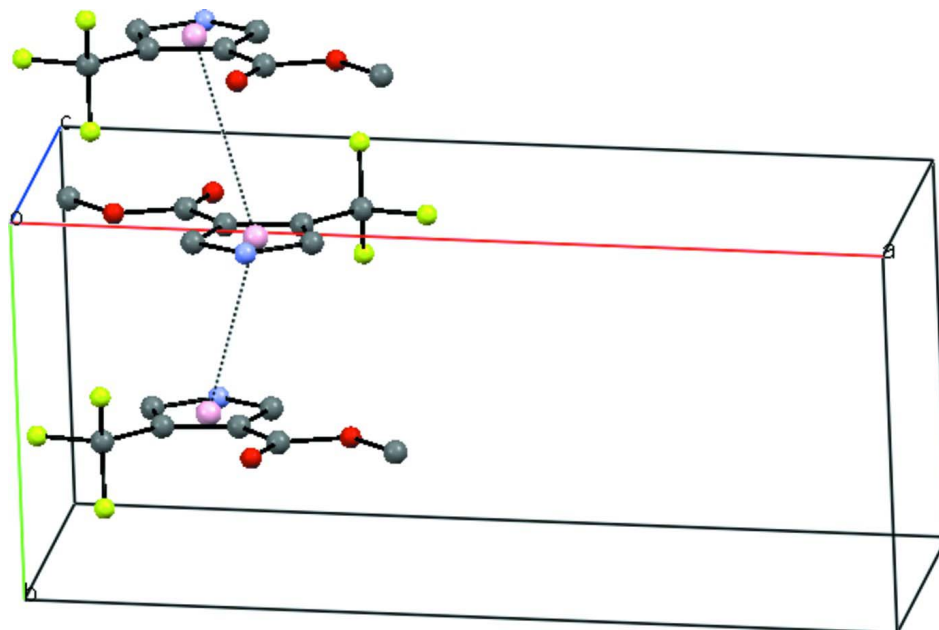
**Figure 1**

Molecular structure of the title compound, showing displacement ellipsoids drawn at the 50% probability level.

Symmetry code for F2a: (x, -y, z).

**Figure 2**

Molecular packing in the title compound displaying $R_2^2(10)$ loops and $C(6)$ chains. H atoms not involved in H-bonding is omitted for clarity.

**Figure 3**

π - π stacking interactions observed in the crystal structure.

Methyl 4-(trifluoromethyl)-1H-pyrrole-3-carboxylate*Crystal data*C₇H₆F₃NO₂ $M_r = 193.13$ Monoclinic, *C2/m*

Hall symbol: -C 2y

 $a = 16.643 (2) \text{ \AA}$ $b = 7.1118 (10) \text{ \AA}$ $c = 6.9618 (11) \text{ \AA}$ $\beta = 98.903 (7)^\circ$ $V = 814.1 (2) \text{ \AA}^3$ $Z = 4$ $F(000) = 392$

prism

 $D_x = 1.576 \text{ Mg m}^{-3}$

Melting point: 405 K

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

Cell parameters from 645 reflections

 $\theta = 3.0\text{--}24.4^\circ$ $\mu = 0.16 \text{ mm}^{-1}$ $T = 293 \text{ K}$

Prism, colourless

 $0.24 \times 0.22 \times 0.20 \text{ mm}$ *Data collection*

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 1.08 pixels mm⁻¹ ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2009)

 $T_{\min} = 0.963, T_{\max} = 0.969$

3752 measured reflections

707 independent reflections

645 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.076$ $\theta_{\text{max}} = 24.4^\circ, \theta_{\text{min}} = 3.0^\circ$ $h = -19 \rightarrow 19$ $k = -8 \rightarrow 8$ $l = -3 \rightarrow 7$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.065$ $wR(F^2) = 0.180$ $S = 1.09$

707 reflections

81 parameters

0 restraints

0 constraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from
neighbouring sitesH atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.1299P)^2 + 0.3175P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$

Extinction correction: SHELXL,

 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.08 (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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
H	0.275 (3)	0.0000	-0.341 (8)	0.073 (13)*	

C1	0.0515 (2)	0.0000	0.2701 (6)	0.0765 (12)	
H1A	0.0456	0.1254	0.3171	0.115*	0.50
H1B	0.0701	-0.0816	0.3777	0.115*	0.50
H1C	0.0000	-0.0438	0.2042	0.115*	0.50
C2	0.18890 (17)	0.0000	0.2149 (4)	0.0436 (9)	
C3	0.24211 (16)	0.0000	0.0673 (4)	0.0391 (8)	
C4	0.21641 (19)	0.0000	-0.1280 (4)	0.0480 (8)	
H4	0.1625	0.0000	-0.1881	0.058*	
C5	0.3504 (2)	0.0000	-0.0863 (5)	0.0563 (10)	
H5	0.4034	0.0000	-0.1137	0.068*	
C6	0.32889 (16)	0.0000	0.0952 (4)	0.0443 (8)	
C7	0.38690 (18)	0.0000	0.2762 (5)	0.0544 (9)	
F1	0.46353 (14)	0.0000	0.2439 (4)	0.1048 (12)	
F2	0.38017 (10)	0.1475 (2)	0.3904 (2)	0.0853 (8)	
N	0.28189 (18)	0.0000	-0.2200 (5)	0.0587 (9)	
O1	0.20994 (15)	0.0000	0.3872 (3)	0.0718 (9)	
O2	0.11034 (12)	0.0000	0.1358 (3)	0.0586 (8)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.057 (2)	0.116 (3)	0.058 (3)	0.000	0.0154 (17)	0.000
C2	0.0503 (16)	0.0517 (15)	0.026 (2)	0.000	-0.0038 (11)	0.000
C3	0.0478 (15)	0.0422 (13)	0.0235 (19)	0.000	-0.0066 (11)	0.000
C4	0.0574 (17)	0.0589 (16)	0.0237 (19)	0.000	-0.0065 (12)	0.000
C5	0.0570 (17)	0.0708 (19)	0.042 (2)	0.000	0.0092 (14)	0.000
C6	0.0491 (16)	0.0483 (14)	0.0331 (18)	0.000	-0.0007 (11)	0.000
C7	0.0481 (16)	0.0667 (17)	0.045 (2)	0.000	-0.0052 (13)	0.000
F1	0.0486 (13)	0.185 (3)	0.076 (2)	0.000	-0.0056 (11)	0.000
F2	0.0959 (13)	0.0903 (13)	0.0570 (14)	-0.0019 (7)	-0.0278 (8)	-0.0240 (7)
N	0.077 (2)	0.0781 (18)	0.020 (2)	0.000	0.0034 (13)	0.000
O1	0.0645 (15)	0.125 (2)	0.0230 (17)	0.000	-0.0013 (10)	0.000
O2	0.0470 (13)	0.0914 (16)	0.0352 (16)	0.000	-0.0006 (9)	0.000

Geometric parameters (Å, °)

C1—O2	1.455 (4)	C4—H4	0.9300
C1—H1A	0.9600	C5—N	1.356 (5)
C1—H1B	0.9600	C5—C6	1.366 (5)
C1—H1C	0.9600	C5—H5	0.9300
C2—O1	1.196 (4)	C6—C7	1.464 (5)
C2—O2	1.338 (4)	C7—F1	1.329 (4)
C2—C3	1.457 (4)	C7—F2 ⁱ	1.332 (3)
C3—C4	1.360 (4)	C7—F2	1.332 (3)
C3—C6	1.427 (4)	N—H	0.84 (5)
C4—N	1.347 (4)		
O2—C1—H1A	109.5	N—C5—H5	125.6

O2—C1—H1B	109.5	C6—C5—H5	125.6
H1A—C1—H1B	109.5	C5—C6—C3	106.2 (3)
O2—C1—H1C	109.5	C5—C6—C7	124.3 (3)
H1A—C1—H1C	109.5	C3—C6—C7	129.5 (3)
H1B—C1—H1C	109.5	F1—C7—F2 ⁱ	105.81 (19)
O1—C2—O2	121.9 (3)	F1—C7—F2	105.81 (19)
O1—C2—C3	126.3 (3)	F2 ⁱ —C7—F2	104.0 (3)
O2—C2—C3	111.8 (3)	F1—C7—C6	112.2 (3)
C4—C3—C6	106.9 (3)	F2 ⁱ —C7—C6	114.12 (17)
C4—C3—C2	125.0 (3)	F2—C7—C6	114.12 (17)
C6—C3—C2	128.1 (3)	C4—N—C5	109.3 (3)
N—C4—C3	108.8 (3)	C4—N—H	119 (3)
N—C4—H4	125.6	C5—N—H	131 (3)
C3—C4—H4	125.6	C2—O2—C1	116.6 (3)
N—C5—C6	108.8 (3)		

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

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N—H ⁱⁱ —O1 ⁱⁱⁱ	0.83 (6)	2.03 (5)	2.810 (4)	156
C5—H5 ⁱⁱⁱ —F1 ⁱⁱⁱ	0.93	2.52	3.442 (4)	171

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